University of Alberta

Polyesters Synthesized from 9-Hydroxynonanoic Acid Derived from Lipid Materials

by

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ABSTRACT

The feasibility of a method based on ozonolysis and hydrogenation reactions for the production of 9-hydroxynonanoic acid from methyl oleate and polyols was demonstrated. Pure 9-hydroxynonanoic acid (9-HNA) was obtained by either recrystallization or silica gel column chromatography. The structure of 9-hydroxynonanoic acid was confirmed by ^{1}H NMR, ^{13}C NMR, FTIR and HR-MS. The methodologies have also been demonstrated to be amenable to 100 gram scales to synthesize 9-hydroxynonanoic acid. 9-hydroxynonanoic acid was converted to 1, 11-dioacycloicosane-2,12-dione (dilactone), which is a potential monomer for synthesis of polyesters. The structure of 1,11-dioacycloicosane-2,12-dione (dilactone) was identified by ^{1}H NMR, ^{13}C NMR, FTIR and GC-MS. Aliphatic polyesters were synthesized via ring opening polymerization of these dilactones. The structure and the number average molecular weight (Mn) of the polyesters were calculated by ^{1}H NMR and GPC. Some physical properties of the polyesters were characterized by DSC and TGA.

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LIST OF ABBREVIATIONS

^{13}C NMR	carbon 13 nuclear magnetic resonance
2D COSY	two dimension correlation spectroscopy
$Al(O^iPr)_3$	aluminum isopropoxide
BH_3-DMS	borane-dimethyl sulfide
$CDCl_3$	deuterated chloroform
CF_3COOH	trifluoroacetic acid
$CHCl_3$	Chloroform
DCC	N, N'-dicyclohexylcarbonyldiimide
DCM	methylene dichloride
Dilactone	1,11-dioacycloicosane-2,12-dione
EDTA	ethylenediamine tetraacetic acid
ESI-MS	electrospray ionization mass spectroscopy
FTIR	fourier transform infrared spectroscopy
GC-FID	gas chromatography-flame ionization detection
GC-MS	gas chromatography mass spectroscopy
GPC	gel permeation chromatography
H_2S	hydrogen sulfide
HBr	hydrogen bromide
HCl	hydrochloric acid
$HfCl_4$	hafnium chloride
HR-MS	high resolution mass spectroscopy
KBH_4	potassium borohydride
$LaCl_3$	lanthanum chloride
$LiBH_4$	lithium borohydride
Lipase CA	candida antarctica lipase

Lipase CR	candida rugosa lipase
Lipase PC	pseudomonas cepacia lipase
Lipase PF	pseudomonas fluorescens lipase
Lipase PP	porcine pancreas lipase
MDSC	modulate differential scanning calorimetry
Mn	number average molecular weight
Mv	viscosity average molecular weight
Mw	weight-average molecular weight
Mz	z-average molecular weight
$NaBH_3CN$	sodium cyanoborohydride
$NaBH_4$	sodium borohydride
NaI	sodium iodide
8-OL	8-octanolide
P (DXO)	poly(1,5-dioxepan-2-one)
P(ε-CL)	Polycaprolactone
PDI	polydispersity index
PEG	polyethylene glycol
pH	power of hydrogen
PHB	poly(β-butyrolactone)
PLA	Polylactide
PLLA	poly(l-lactide)
P-TsOH	p-toluenesulfonic acid
PVL	poly(pivalolactone)
$RhCl(PPh_3)_3$	rhodium tris-(triphenylphosphine) chloride
ROP	ring opening polymerization
SEC	size exclusion chromatography
$Sn(Oct)_2$	tin (II) bis(2-ethylhexanoate)
T_g	glass transition temperature

TGA	thermal gravimetric analysis
THF	Tetrahydrofuran
TLC	thin layer chromatography
T_m	melting temperature
TMC	trimethylene carbonate
$Zn(DMH)_2$	zinc bis(2,2-dimethyl-3,5-heptanedionate-o, o')
β-BL	β-butyrolactone
β–PL	β-propiolactone
δ-VL	δ–valerolactone

Chapter 1 Literature review

1.1 Ozonolysis and hydrogenation of fatty acids

1.1.1 The importance of 9-hydroxynonanoic acid

Omega-Hydroxyl fatty acids are part of a family of molecules which possess two functional groups located at the two ends of the fatty acid chain, as shown by their generalized structure, represented in Figure 1. The hydroxyl and carboxylic acid functionalities make such molecules useful intermediates in both laboratory and industrial scale synthesis (1).

A number of omega-hydroxyl fatty acids have been found to occur in small amounts in natural substances, such as in hog liver and the royal jelly of honey bees (a nutritious substance secreted by of worker bees) (2). Omega-hydroxyl fatty acids are interesting from several standpoints: they are used in the preparation of mixed diesters e.g. methyl 9-acetoxynononoate, ethyl-acetoxynonanoate, n-propyl 9-acetoxynononoate and n-butyl 9-acetoxynononoate, which are potential reactants in transesterification reactions (3). They can also be applied in the preparation of comparably longer chain diesters, which are extensively used in cosmetic formulations (4). Ω-hydroxyl fatty acids are also intermediates in the synthesis of phospholipids, which have been used as membrane model systems for investigating biochemical interactions (2). In addition, they are valuable intermediates for the synthesis of very useful large-membered lactones, some of which exhibit flavour properties or are useful monomers for the synthesis of biodegradable polyesters (5). 9- hydroxynonanoic acid, a 9-carbon omega-hydroxyl fatty

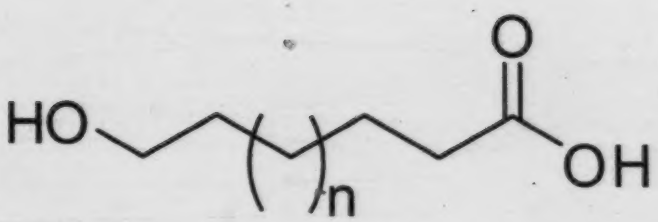


Figure 1: Basic structure of omega-hydroxyl fatty acids; n is the number of methylene group

acid was found to be linked to larger molecules, such as pseduomonic acids (*via* an organic reaction) to produce pseudomonic acid A, which is a compound that exhibits antibiotic activity (6). More recently, it has been found that omega-hydroxyl fatty acids are the major component of the natural polymer, suberin, which is found in the epidermis, endodermis and root phellem of some plants e.g. fern frond plants (7). It is also an important substance involved in the wound healing of the aerial parts of some plants, such as fern frond plants (8).

1.1.2 Methodology for the synthesis of 9-hydroxynonanoic acid

Ozonolysis and hydrogenation reactions used to produce alcohol products have been fully reviewed in 2003 by Rubin (9). However, it is necessary to review these reactions in more detail for this research project. There have been a variety of methods published regarding the synthesis of 9-hydroxynonanoic acid (1, 3, 10-16) based on ozonolysis and hydrogenation techniques. Previous experiments have indicated that the production of the desired product, 9-hydroxynonanoic acid, was affected by the selection of starting materials, and resulted in varying results. Sousa *et al.* (12) found that the ozonolysis of oleic acid followed by a reduction with sodium borohydride, produced 9-hydroxynonanoic acid with a low yield of 46 % . In 1986, Pascal and coworkers (14) found that when azelaic acid mono-methyl ester was subjected to ozonolysis conditions, followed by a lithium borohydride ($LiBH_4$) reduction, the yield of 9-hydroxynonanoic acid was relatively high at 75 %. However, due to the high cost of $LiBH_4$ it was not a suitable option for use in large scale synthesis. In 1989, Flippin and coworkers (15)

found that the ozonolysis of methyl ricinoleate and its subsequent reduction with borane-dimethyl sulfide (BH_3-DMS), resulted in the production of 9-hydroxydecanoate with a yield of 96 %. The high cost of BH_3-DMS and the number of steps involved in this process and the production of H_2S gas as a by-product made this process unfeasible for large scale production and also raised environmental concerns.

In 1999, Kula's group (3) reported a procedure involving ozonolysis followed by an electrochemical-reduction of methyl ricinoleate. This methodology produced 9-hydroxynonanoic acid with a high yield of 98 %, but unfortunately the electro-reduction process was time consuming and therefore not suitable for scale up operations.

In 2005, Narine and co-workers successfully utilized a modified method to produce polyols from canola oil *via* an ozonolysis and hydrogenation technique. This method can be used for scale up production (17).

1.2 Lactones and dilactones

1.2.1 Properties and importance of lactones

Lactones are cyclic esters and are usually formed from the intramolecular condensation reaction of an alcohol with a carboxylic acid functional group. The general structure for a lactone is shown in Figure 2. To indicate its ring size, prefixes are attached to the name of the lactone. For example, with some alkyl substituted lactones, the prefixes beta (β), gamma (γ) or delta (δ) are used to denote a 4-membered, 5-membered or 6-membered ring lactone respectively.

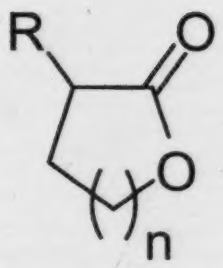


Figure 2: Basic structure of a lactone: R = H or an alkyl group; n = number of methylene groups

Some of the β-, γ-, and δ-lactones are flavour and aroma constituents in many natural products such as fruits (18). For example, bovolide (19), a novel gamma lactone (2,3-dimethyl-4-hydroxynona-2,4-dienoic acid) which has been isolated from butter, is an important flavour compound and has been patented to improve the flavour of tobacco (20). In addition, some synthetic lactones, specifically γ-lactone stereoisomers have also been shown to be important flavors compounds (21, 22). As an example, 4-alkyl-substituted γ-lactones or 3, 4-dialkyl-substituted γ-lactones can be used as important intermediates in the total synthesis of organic natural products. Alternatively, lactones or dilactones can be used as potential monomers for the synthesis of either polyesters or polylactones.

1.2.2 Synthesis of lactones, in particular nonanolactone

A number of different starting materials can be used in the chemical production of lactones. Traditionally, ketones have been used as a starting material in the Baeyer-Villiger oxidation reaction to produce lactones (23). Lactones can also be produced from the intramolecular condensation reaction of hydroxyl fatty acids, usually initiated with a Lewis acid catalyst (24). Some literature also reports that N, N'-dicyclohexylcarbonyldiimide (DCC) can be used to react with some types of hydroxyl fatty acids to form lactones (25), and cyanuric chloride can be used as a catalyst to convert 6-hydroxyl fatty acids to the corresponding lactones (24).

Nonanolactone is an important intermediate for organic synthesis; it is also a useful monomer for producing aliphatic polylactones particularly by ring opening polymerization. There are also a few published methods for the production of

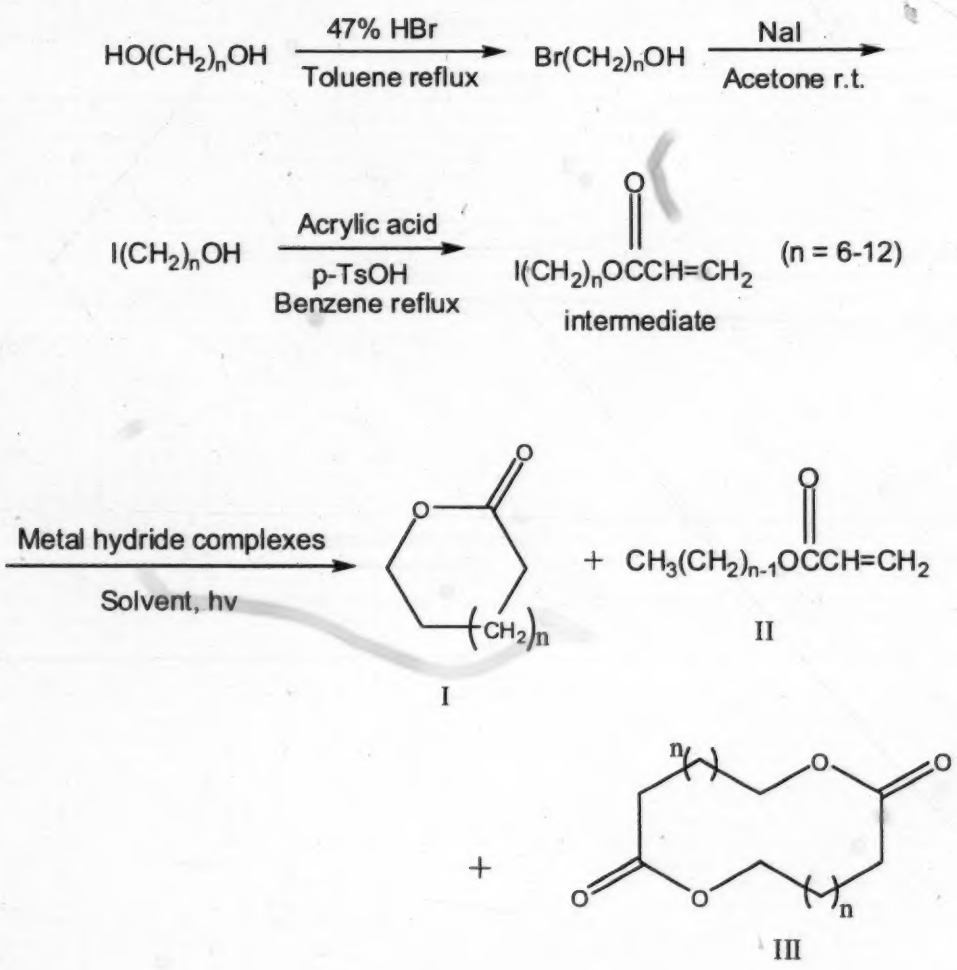
nonanolactone from 9-hydroxynonanoic acid. The first attempt to synthesize nonanolactone from 9-hydroxynonanoic acid occurred in 1965. The reaction was carried out in benzene and catalyzed by *para*-toluenesulfonic acid, however, the experiment resulted in the production of a dilactone with a yield of 32 % instead of nonanolactone (26). In order to produce the desired nonanolactone with a higher yield, further research work was conducted by several other researchers, such as the groups of Kellogg, Kurata and Yamamoto.

In 1981, Kellogg and coworkers (27) developed a method to produce lactones from long chain fatty acids possessing a good leaving group, such as omega-iodo fatty acids. It was found that for the long chain fatty acids particularly when the carbon number is more than 9, the corresponding monolactones can be produced with a yield ranging from 23 % to 85 %. Some dilactones were also obtained. However, when 9-hydroxynonanoic acid was used as the starting material, no monolactone was obtained; instead a dilactone was obtained as the product. In 1993, Mukaiyama's research group (28) reported a new method to produce nonanolactone from 9-hydroxynonanoic acid, using *p*-trifluoromethylbenzoic anhydride and a catalytic amount of Lewis acid. However, the yield of nonanolactone was only 33 % and that of the obtained undesired dilactone was 47 %. Four years later, Mukaiyama *et al.* reported an alternative method to synthesize nonanolactone with an isolated yield of 74 % (29). This method involves treatment of 9-hydroxynonanoic acid with 1, 2-bisdimethylsilylbenzene and a $RhCl(PPh_3)_3$/ dimethylsilylbis(trifluoromethanesulfonate) catalyst. Nonanolactone was obtained with a yield of 87 %, additionally, only 8 % of the undesired dilactone was

obtained (30) in comparison to the previous method in 1993 (28) which produced nonanolactone in 33 % yield.

In 1994, Kurata and coworkers (29) published a method to produce lactones that involved using hydrogen bromide (HBr), sodium iodide (NaI), acrylic acid and *para*-toluenesulfonic acid (*p*-TsOH) to produce an intermediate (shown in Scheme 1) which was then reacted with a metal hydride such as sodium cyanoborohydride ($NaBH_3CN$), sodium borohydride ($NaBH_4$), or potassium borohydride (KBH_4) to produce the desired lactones. For example, the results for producing 14 membered ring lactones (n=10) are depicted in Scheme 1 and the yield of different compositions are shown in Table 1. It was also found that using $NaBH_3CN$ in this reaction led to the monolactone product being obtained with the highest yield. When $NaBH_4$ and KBH_4 were used, the monolactone yields decreased from 87 % to 43 %, and with lithium aluminum hydride $(LiAlH)_4$ as the catalyst, no monolactone was obtained (29). The reason is that $LiAlH_4$ is a strong reducing reagent so the iodide reacted with the hydride before the generated alkoxide had chance to displace the iodine to form the cyclized product. In another case, when a photocyclization reaction involving $NaBH_3CN$ was used, omega–iodoalkylacrylate was converted to nonanolactone with a yield of 74 %.

In an effort to produce nonanolactone with higher yields, Yamamoto's group undertook further research and in 1996 developed new methodology that produced nonanolactone with a relatively high yield of 87 % and only 5 % of the undesired dilactone. (31). These results were obtained with the use of the expensive catalyst, scandium trifluoromethanesulfonate. Additionally, this process was found to be very



Scheme 1: Synthesis of lactones from omega-hydroxyl fatty acids (Abe et al., 1994)

Table 1. Different metal hydride complexes reacting with omega-hydroxyl fatty acids and the effect on the selectivity of product (Abe et al., 1994)

Reagent	Selectivity [b]/%			
	I	II	III	Others [c]
$NaBH_3CN$	87	1	12	-
$NaBH_4$	53	19	14	14
KBH_4	43	19	17	21
$LiAlH_4$	-	-	-	100

[a]: Reaction condition: 10-iododecylacrylate: 1mmol; reagent, 5mmol; solvent: 400 ml; reaction time: 3 hours; room temperature.

[b]: Determined by GC analysis.

[c]: Reduction product.

time consuming even with the use of a mechanically driven syringe pump to add the starting materials.

In 2002, Yamamoto *et al.* reported an efficient method to synthesize some esters or polyesters using such catalysts as hafnium chloride (IV), or esters with zirconium chloride (IV). Both of these catalysts are commercially available and efficiently catalyze ester formation (32) with high yields. However, in the case of producing polyester, it was found that hafnium chloride has significantly higher catalytic activities for some kinds of hydroxyl fatty acids in converting them to polyesters. Table 2 illustrates the products that were synthesized from different hydroxyl fatty acids when catalyzed by hafnium chloride. Yields of both lactone and polyester were more than 88 % and the maximum yield obtained was 98 %. According to the results listed in Table 2, it was found that some hydroxyl fatty acids having relatively long chains can form polyester products; however, for other hydroxyl fatty acids with relatively short chains, lactones were obtained.

1.3 Synthesis and properties of polyesters

Polyesters are used widely throughout the chemical industry and our daily lives. Polyesters can be divided into two main categories: a) non-biodegradable and b) biodegradable. Various types of non-biodegradable polyesters, particularly polyethylene terephthalate and polycarbonate, have been used in the manufacture of high performance aircraft enclosures, commodity and engineering plastics, and beverage, food and other liquid containers (33, 34). Biodegradable polyesters, especially aliphatic polyesters such as polycaprolactone (P(ε-CL)) and polylactide (PLA), have been widely used in medical applications such as drug delivery systems due to their environmentally friendly

Table 2. Products obtained from the catalyzed direct esterification reactions of different hydroxyl fatty acid starting materials (Ishihara et al., 2002)

Starting material	**Solvent (reflux)**	**Catalyst [a] (mol%)**	**Esterification product**
$HOOC(CH_2)_4OH$	toluene	0.2	lactone
$HOOC(CH_2)_5OH$	toluene	0.2	lactone
$HOOC(CH_2)_9OH$	xylene	0.2	polyester
$HOOC(CH_2)_{11}OH$	xylene	0.2	polyester
$HOOC(CH_2)_2CO_2(CH_2)_6OH$	xylene	0.2	polyester
$HOOC(CH_2)_7CO_2(CH_2)_{10}OH$	xylene	0.2	polyester
$HOOCPhCO_2(CH_2)_{10}OH$	xylene	1.0	polyester

a: Hafnium chloride ($HfCl_4$) was used as catalyst.

properties and their compatibility with human tissues (35). In 1960, it was initially proposed by Polistina that poly(L-lactide) (PLLA) had the potential characteristics of biocompatibility, biodegradability and bioresorbability. After this discovery, significantly more research was conducted on the homopolymers of PLA and the copolymer of lactide and glycolide which forms the basis of surgical sutures, drug delivery devices and various body implants (36).

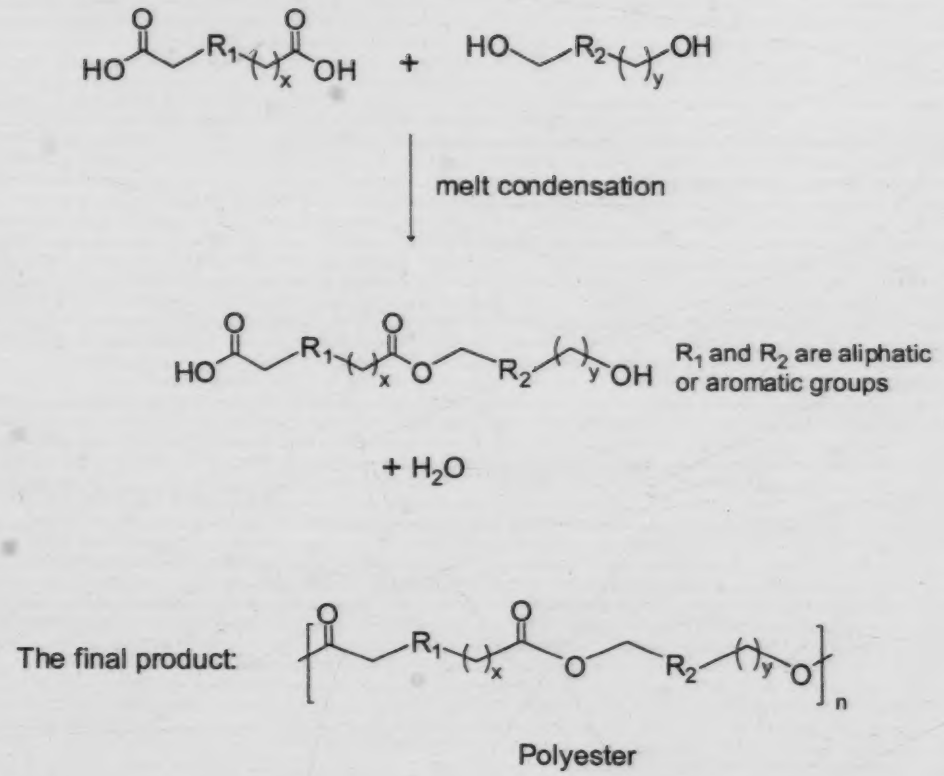
Aliphatic polyesters are important materials. Some of these polyesters, such as PLA and P(ε-CL), possess special properties, such as compatibility, permeability or biodegradability, which make them especially suitable for agriculture, industrial and medical applications (37). Other aliphatic polyesters such as polyethylene glycol (PEG) and poly(1,5-Dioxepan-2-one) (P(DXO)) are also very important polymers in medical research. This is because they are hydrolytically unstable and degrade in vitro and vivo (38) without the release of toxic by-products. P(ε-CL), which has a low glass transition temperature (T_g) and high permeability, is one of the most frequently used compounds in drug delivery systems. It has also been used as biodegradable container material (39, 40). Outside the field of medicine, P(ε-CL) can be blended with starch to produce several derivatives which have been used in the manufacture of shopping bags (35, 41). Homopoly(DXO) is an amorphous material with low T_g (approximately -36°C), which undergoes hydrolysis in vitro (42) and is therefore a possible candidate to be used in the design of bioabsorbable materials. Many methodologies have been developed around the production of polyesters, which has allowed them to be utilized in a variety of fields and research areas.

1.3.1 Melt condensation reactions

The melt condensation reaction is a process in which two molecules are joined together under the conditions of high temperature and low pressure. Usually this process involves the loss of small volatile molecules, such as water or hydrogen chloride. Another situation termed polyaddition, occurs when two molecules are joined together without the elimination of any other molecules. A variety of step-growth polymerization reactions are called condensation polymerization, and thus the products are referred to as condensation polymers (43).

Traditionally, polyesters have been synthesized using the melt condensation reaction. The monomers used in this reaction are typically diols and diacids or some kind of hydroxyl fatty acid (44). The general structure of polyesters synthesized with the melt condensation reaction is depicted in Scheme 2.

Other previously utilized methods for the synthesis of different polymers from monomers with different functional groups include vacuum-melt, purge gas and azeotrope conditions. These methods were found to be limited and impractical due to the fact that they did not produce polymers (45). Therefore, it is necessary to develop more advanced and applicable methods to synthesize polyesters. Other methodologies that can be used to make polyesters include addition of acid catalysts or other additives to activate the carboxylic acid functionality and facilitate the esterification process. Some phase transfer catalysts (46) and environmentally friendly processes have also been previously reported (47).



Scheme 2: A traditional melt condensation reaction to produce polyester

1.3.2 Catalyzed reactions and the use of more reactive reagents

Instead of carrying out direct melt condensation of diols and diacids, the condensation of diacid derivatives (e.g. acylchlorides or esters) with diols can also achieve a positive result. The use of catalysts such as acids, bases or transition metal complexes also achieves similar results. However, catalyst residues can have undesirable side effects. In order to minimize these side effects, trace amounts (i.e. low concentrations in ppm) of catalysts such as titanium, tin, antimony or hafnium are used to synthesize polyesters (32). These catalysts are able to produce polyesters with desired average molecular weights.

Generally, the carbonyl groups of carboxylic acids are less reactive than those of the acylchlorides because of the electron withdrawing effect of the chloride atom. During the reaction process, hydrochloric acid side products can be efficiently removed from the reaction to push the equilibrium forward toward obtaining more products. Alternatively, trifluoroacetic acid and silyl chloride have also been used to activate the carboxylic acid, since they can work as efficiently as the above method. Catalysts can be easily separated from the products; however; they are expensive and are only suitable for small scale production.

1.3.3 Ring opening polymerization (ROP) to produce polyesters

Ring opening polymerization (ROP) is similar to addition polymerization. Ring opening polymerization occurs at the end of a growing chain where it acts as a reactive center upon which other monomers can react to propagate the chain. In ring-opening

polymerization, the monomer is a cyclic compound and the chain typically propagates through cationic or anionic propagation.

In the case of aliphatic hydroxyl fatty acids with medium chain lengths (e.g. 8, 9 and 10 carbon hydroxyl fatty acids), it is very difficult to synthesize polyesters by using the melt condensation reaction using hydroxyl fatty acid monomers or diols and diacids as the starting materials. In order to efficiently synthesize polyesters, one solution would be to use cyclic monomers. Therefore, monomers such as hydroxyl fatty acids need to be converted into lactone or dilactones first prior to ROP in order to produce the target polymers. ROP can provide more convenient routes to synthesize target polyester or polylactone polymers in comparison to using traditional step polymerization methods. (48-50)

1.3.3.1 Aluminum or zinc catalysts

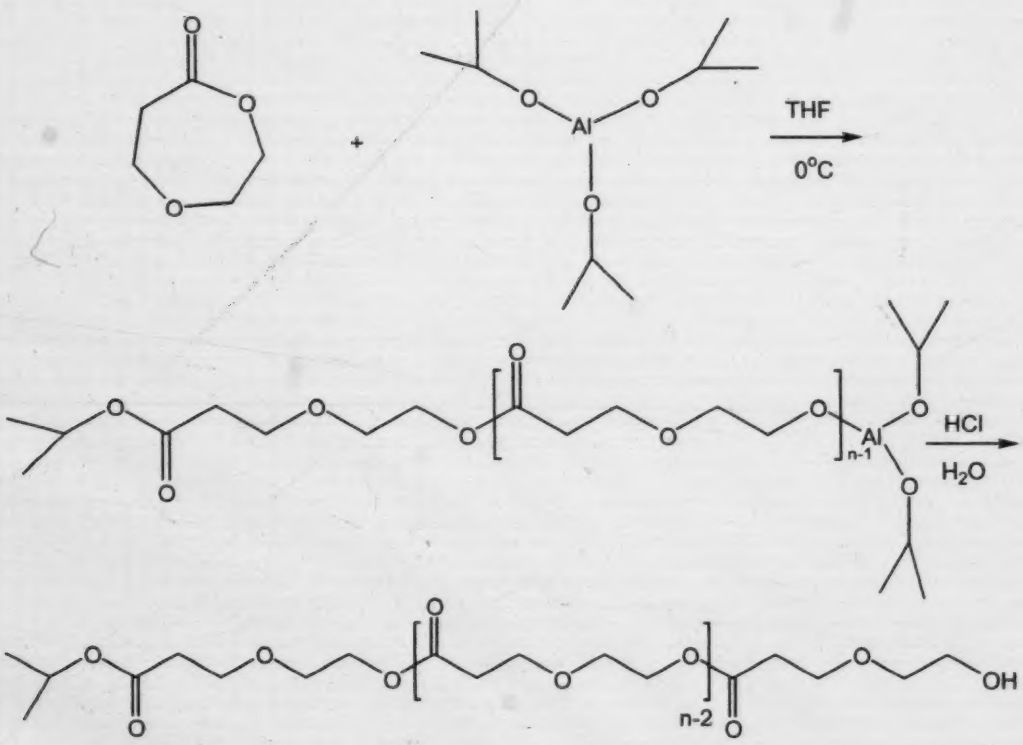
Hamitou, A. *et al* (51), Ouhadi, T. *et al* (52), and Heuschen, J., et al. and Teyssie, P. (53) reported that bimetallic (Al-Zn) μ–oxo-alkoxides were very effective in the controlled polymerization of unsubstituted lactones. Feng and Song (54) later showed that living polymerization of lactones could be extended to D, L-lactide. Inoue *et al.* (55, 56) were also able to polymerize lactones and lactides by using (α,β,γ,δ-tetraphenylprophinato) aluminium alkoxides as initiators. In 1992, Terome's research group (57) found that when aluminium isopropoxide was used as the catalyst, lactides (D,L and L,L) can be polymerized and a controlled molecular weight PLA can be synthesized. A few years later, the same methodology was applied to synthesize a homopolymer of poly(1,5-Dioxepan-2-one) P(DXO) and a copolymer of P(DXO) with

P(ε-CL) (58). The general synthetic route catalyzed by aluminium isopropoxide is shown in Scheme 3.

In order to investigate whether aluminium alkoxides were functional or not, Terome's research group polymerized ε-CL using two different solvents: THF and toluene. It was found that the polymerization reaction in toluene was faster than that of THF, presumably, this is due to competition between monomer and solvent for coordination to the aluminium metal centre. As a result, toluene was determined to be a good solvent in the synthesis of P(ε-CL) (59). Additionally, using aluminium isopropoxide as the catalyst has a number of advantages. It is inexpensive, cost effective, and the entire reaction is relatively easy to manipulate. The reaction's by-products are non-toxic and the process is suitable for large scale synthesis. However, there are instances where the aluminium alkoxide has generated polyesters with low polydispersity indices (60). Some zinc catalysts have also been reported to be as highly efficient as aluminum for use in ROP (61-63). However, they are not commercially available catalysts and due to the long preparation time are not suitable for scale up synthesis.

1.3.3.2 Tin compounds

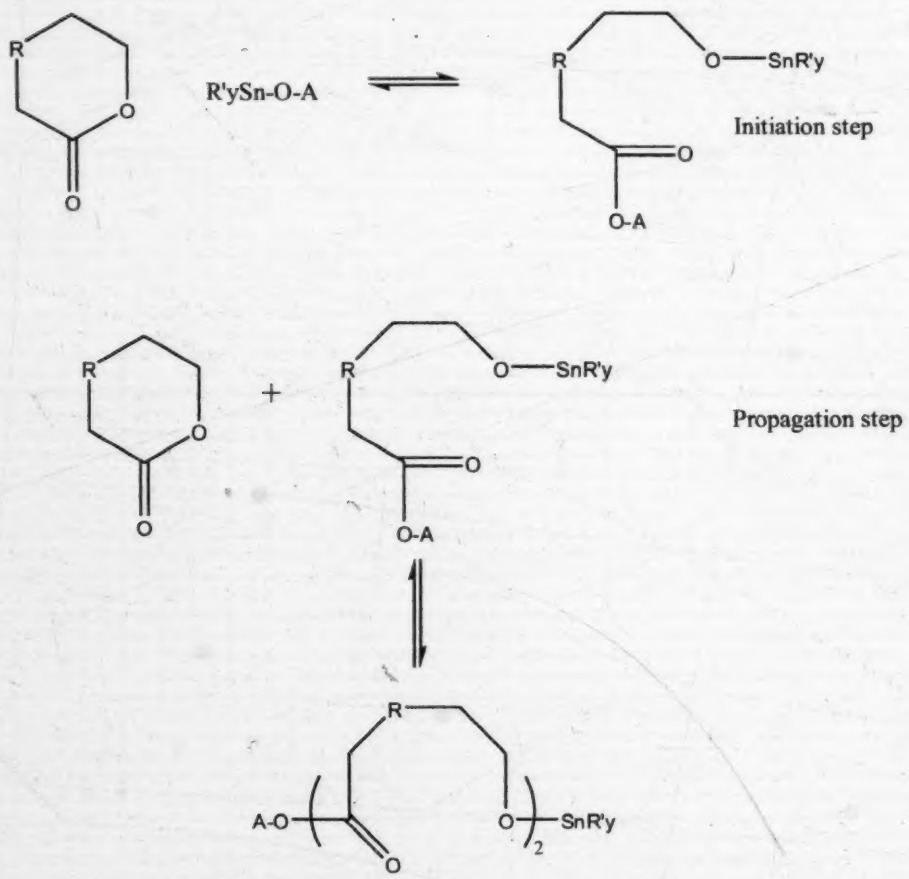
Tin alkoxides and phenyl tin alkoxides have been reported to be efficient initiators for the ring opening polymerization of various lactones and lactides (64, 65). It was found that these compounds not only acted as initiators with lactones but they were efficient transesterification catalysts for acyclic esters. Thus, they may cause intensive degradation of polylactones at elevated temperature. In order to avoid degradation during



Scheme 3: Aluminum isopropoxide catalyzed ring opening polymerization of (1,5-dioxepan-2-one) (Lofgren et al., 1994)

the polymerization process, Pennings' group (66) studied the kinetics of the L-lactide bulk polymerization with alternative catalysts: tin (II) bis(2-ethylhexanoate) ($Sn(Oct)_2$), and zinc bis(2,2-dimethyl-3,5-heptanedionate-O,O') ($Zn(DMH)_2$). It was found that the physical properties of the obtained PLA depended strongly on the catalysts (66). With conversions beyond 80 %, the zinc catalyst had a higher rate of polymerization than that of the tin catalyst. However, the molecular weight was not proportional to the conversion, which may have resulted from the fact that one molecular catalyst initiated two living polymer chains. The reaction mechanism is shown in Figure 3. There are two main steps in the ROP reactions enabled by tin: initiation and propagation. In the initiation step, the tin complex attacks the lactone to achieve a ring opening for the formation of a living chain. In the propagation step, one more lactone molecule reacts with the living chain to propagate the reaction.

Further study was undertaken in 1988 by Kricheldorf's group (65) in an effort to discover more efficient initiators for ROP. A few heterocyclic tin complexes were developed and utilized as catalysts for the ROP reaction. The application of these catalysts resulted in the synthesis of polyesters with tailored molecular weights. For example, L-lactides were polymerized when the ROP was catalyzed by cyclic Bu_2Sn (derived from 1, 2-ethanediol or 2-mercaptoethanol) and high molecular weight PLA was obtained (67). It was found that the molecular weight was strongly dependent upon the ratio of monomer to the initiator, the higher the ratio of monomer to the initiator - the higher the molecular weight of the product. Also, the longer the reaction time, the higher molecular weight of the product was obtained.



A = an alkyl group and R' = other groups bound to Sn.

Figure 3: Initiation and propagation mechanism of lactone with a tin alkoxide catalyst (Nijenhuis et al.,1992)

The reaction was found to be unsuitable for large scale synthesis since it was carried out at 120°C and the tin complex is highly toxic in comparison to other initiators. An example of the initiation and propagation mechanism (66) is shown in Figure 3.

1.3.3.3 Rare earth metal catalysts

There are several reports within the literature about rare earth metal catalyzed polymerization of lactones and trimethylene carbonate (TMC), for instance, $(C_5Me_5)_2SmH(THF)$ and $(C_5Me_5)_2SmCH_3(THF)$ are rare earth alkoxide complexes which are used as initiators of ROP. In 1997, Shen's research group (68) found that rare earth halides can catalyze the ROP of ε-CL and TMC. Rare earth halides show high activities for the polymerization of TMC, but show low activities for that of ε-CL. The mechanism (68) of ROP for ε-CL catalyzed by $LaCl_3$ is indicated in Figure 4.

There are 3 steps to complete the ROP of ε-CL. The first step involves the reaction of CL and $LaCl_3$ to produce rare earth ε-chlorocaproate (1) by ring cleavage of ε-CL and chlorine-transfer from $LaCl_3$ to ε-CL, this is shown in Figure 4 (a). In the second step, the produced rare earth metal caproate further initiated the propagation of ε-CL into the ε-chorocaproate bond, as is shown in Figure 4 (b). The third step involves the use of trace amounts of water to initiate the polymerization. The hydroxyl fatty acid is then produced by ring opening of the caprolactone, which has the same function as the trace water. The whole mechanism of the third step is an activated-hydrolysis mechanism, as is shown in Figure 4 (c). In addition, for some catalysts such as $DyCl_3$ and $LaCl_3$, the conversion is no more than 50 %.

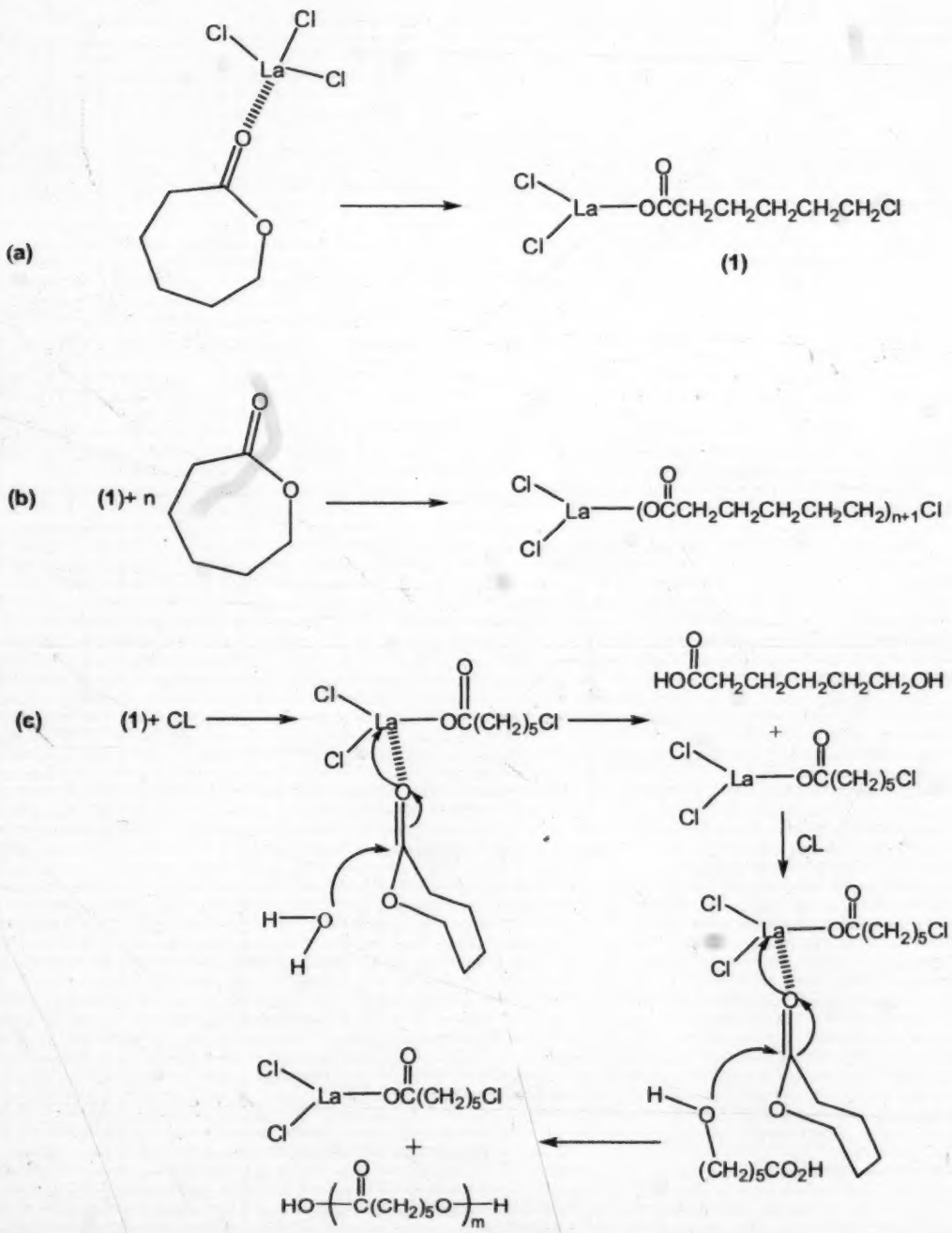


Figure 4: $LaCl_3$ catalyzed ring opening polymerization of ε-CL (Shen et al., 1997)

The literature reports that backbiting reactions (either an intramolecular reaction or a polymer chain scission reaction used to form oligomers) are dependent on the metal compound used as initiators as well as on the ligands surrounding them (66, 69) e.g. aluminium alkoxide generated polyesters with low polydispersity indices. (56, 60) In order to develop a relatively easy method to synthesize polylactones with high polydispersity indices *via* ROP, Agarwal's group (69) designed a new catalyst for living polymerization. The new catalyst consisted of bulky ligands shielding the active centre from the growing polymer chain, therefore reducing transesterification reactions (69). Generally, organolanthanide complexes seem to be highly active and well suited as initiators for the ROP of lactones due to their high Lewis acidities. Moreover, the rare earth metal has the advantage of its large size making it suitable for the synthesis of a catalytic complex with bulky ligands (69).

1.3.3.4 Lipase catalysts

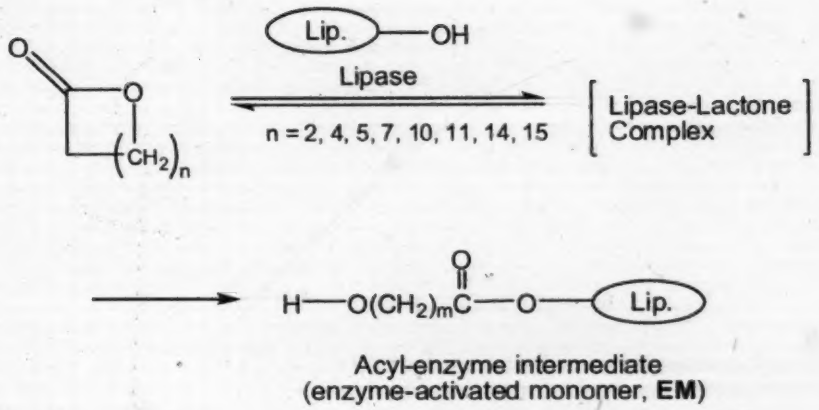
Lipases are enzymes which can be used as catalysts and can also be utilized for in vivo reactions not only of natural substrates but also of some synthetic ones. Typical characteristics of enzyme catalysts include high catalytic activity, a large rate acceleration of the reaction under mild conditions, a high selectivity of substrates and reaction modes, and no formation of by-products (70). Some natural lipases, such as phosphatidyl choline and co-enzyme A, play essential roles in biosynthetic pathways and the reactions occurred in water environment. Phosphatidyl choline is a precursor of desaturase, which can oxidize saturated fatty acid chain in the triglycerides backbones to produce more unsaturated fatty acid. Co-enzyme A works as transesterification catalyst and makes it

possible to produce a variety of esters in the biosynthesis. (71) Other synthetic enzymes, such as *Candida rugosa* (Lipase CR) and *Candida antarctic* (Lipase CA), can be used in organic solvents with relatively low temperature, and can catalyze esterification to produce polyesters. These enzyme catalysts have provided a new synthetic strategy for the production of useful polymers, most of which are difficult to produce with conventional chemical catalysts. In enzymatic polymerization, polymers can be obtained under mild reaction conditions without using a toxic reagent. Therefore, enzymatic polymerization has large potential to be used as an environmentally friendly synthetic process for polymeric materials. This provides a good example of a method for achieving "green polymer chemistry".

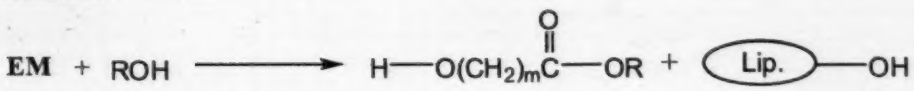
The use of a lipase catalyzed ROP reaction to synthesize polyesters first appeared in 1993 and was carried out by Kanai and Uyama. (72, 73) After the establishment of this process, a variety of cyclic compounds, which included 4- to 17-membered ring lactones were reported to be polymerized by lipase catalysts (74-77). Among them, lipase catalyzed polymerization of lactones has been most extensively investigated. The structures of the lactones, their polymerization products and possible mechanisms are shown in Figure 5. Among them, β-propiolactone (β–PL) was polymerized using *pseudomonas* family lipases as a catalyst, yielding a mixture of cyclic oligomers with a molecular weight of several hundred (75). When ROP of (β-PL) was catalyzed by the *Candida rugosa* (Lipase CR), a high molecular weight poly (β-PL) was obtained with a weight-average molecular weight (Mw) of greater than 50,000 g/mol using only a small amount of lipase CR (0.5% for the monomer) (78, 79). The lipase catalyst also induced the polymerization of β-butyrolactone (β-BL) to give poly (β-BL) (PHB) (80). The

molecular weight of PHB can reach 7300 in the polymerization reaction catalyzed by *Porcine pancreas* lipase (PPL) at 100°C. Lipase CR also showed high catalytic activity toward this polymerization at high temperature. However, the resulting product contained a large amount of cyclic oligo(β-hydroxybutyrate). The cyclic oligo(β-hydroxybutyrate) was also obtained in the lipase-catalyzed reaction of linear PHB (81) and δ–valerolactone (δ-VL) (28, 82, 83). The number average-molecular weight (Mn) of the enzymatically obtained polymer was relatively low (less than 2000).

E-CL has also been subjected to enzyme catalyzed polymerizations with different types of lipases including Lipase PPL, Lipase CR, *Pseudomonas fluorescens* lipase (lipase CF) and lipase PC. It was found that with lipase PF, more than 40 mol % of the catalyst was required to induce polymerization (70, 82). On the other hand, with lipase CA, only 1 mol % of the catalyst was required to achieve a satisfactory result (84). Polymerizations, in general, produced linear polymers but in organic solvents, the main product obtained is a cyclic structure which could result from an intramolecular condensation reaction (85, 86). In 2000, Kumar's group found that lipase CA can catalyze ε-CL to produce polymers. In addition, it was found that lipase CA could be reused in a further five polymerization cycles without the catalytic activity changing (87). Nine-membered ring lactones such as 8-octanolide (8-OL) can be enzymatically polymerized as shown in1998 by Uyama's group. It was found that lipase CA and lipase PC showed high catalytic activity during the polymerization process (77). However, the literature does not contain information regarding the ROP of nonanolactone or 1,11-dioxacycloicosane-2,12-dione (a dilactone).



Initiation:



Propagation:

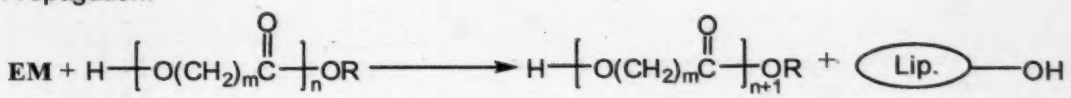


Figure 5: Enzymatic ring opening polymerization of unsubstituted lactones (Uyama et al., 1995)

1.3.4 Chemical and physical properties of polyesters

The chemical and physical properties of aliphatic polyesters and polylactones are normally identified by structure, molecular weight, thermal transition, thermal degradation and biodegradability.

1.3.4.1 Molecular weight

Molecular weight value is one of the most important parameters which influence the properties of polyesters and polylactones. Much of the literature has reported on how to define the molecular weight of polymers and on the various methods that can be used for measuring molecular weights (43, 88-90). Molecular weights are most often reported as the number average molecular weight (Mn), the weight average molecular weight (Mw), the viscosity average molecular weight (Mv) and the z-average molecular weight (Mz) (89). The measurement techniques which are most commonly used for measuring the molecular weights of polymers include end-group analysis according to ^{1}H NMR, gel permeation chromatography (GPC) (or size exclusion chromatography (SEC)), light scattering and solution viscometry. Mn values can be obtained by ^{1}H NMR according to the end-group; however, it has been found that the Mn value obtained with ^{1}H NMR is lower than that obtained with GPC (58, 72). Some of the molecular weight values obtained with ^{1}H NMR are only 50 % or 30 % of those obtained from GPC (58, 91). Comparison of the two measurements shows that the molecular weight obtained from GPC is more accurate than that obtained from ^{1}H NMR because GPC measures the

polymer's size, while ^{1}H NMR calculates the molecular weight according to the integration of the polymer's terminal groups.

The physical properties of polymers are primarily determined by the molecular weights and chemical compositions. The degree of polymerization is used as a parameter to evaluate the number of repeating units in a polymer's backbone, thereby generating a value that is proportional to the molecular weight. The polydisperity index (PDI) is another measurement parameter for polymers, which can be obtained by the ratio of weight average molecular weight to number average molecular weight (Mw/Mn). For homopolymers, the theoretical polydispersity index is 1.0 (89).

The following are a few examples of polyesters which are composed of different compositions. For example, Table 3 shows the molecular weight values and PDI for the homopolymer of P(DXO). Table 4 shows the molecular weight values and PDI for the copolymer formed from P(ε-CL) and P(DXO) initiated by aluminium isopropoxide. The data contained in Table 3 indicates that the greater the monomer to initiator ratio, the higher the resulting molecular weight value. Also, the higher the molecular weight value, the higher the T_g obtained. Thus, it provides a guideline for the production of polyesters with tailored molecular weights or T_g's. In addition, the molecular weight values obtained from the ^{1}H NMR are smaller than those obtained from GPC, which can be seen in both Tables 3 and 4.

1.3.4.2 Thermal properties

Differential Scanning Calorimerty (DSC) is one of the methods used to measure a polymer's thermal properties, particularly crystallinity, melting temperature (T_m), glass

transition temperature (T_g) and enthalpy change. When polymers are made up of different compositions, their thermal property results will be different. Taking homopolymer P(DXO) as an example, when the thermal properties of this homopolymer were determined by DSC, the process gave only one T_g, as the T_g of the P(DXO) was increased, the molecular weight increased (shown in Table 4). As for a copolymer such as Poly(ε-CL-b-DXO) (58), which was composed of 63 % P(ε-CL), there were two T_gs as shown in Figure 6 (the lower curve). One T_g was found at -55 °C and the other was at -40 °C. The T_g of the homopolymer of P (ε-CL) was -65 °C which is shown in Figure 6 (the upper curve). The T_g of the P (ε-CL) block in the copolymer was higher than that of the P (ε-CL) homopolymers. In addition, the T_g of the copolymer can be calculated according to the equation:

$$\frac{1}{Tg_m} = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2} \qquad \text{Equation (1)}$$

Where the T_{gm} is the glass transition temperature of random copolymer; w_1 and w_2 are weight fraction of homopolymers 1 and 2 and T_{g1} and T_{g2} are the glass transition temperatures of homopolymers obtained from monomer 1 and monomer 2, respectively. The unit of T_g used here is Fahrenheit.

Thermal degradation of polymers is important to characterize, and this is done with the use of a thermogravimetric analyzer. The thermal degradation of some polylactones such as PLA, poly(pivalolactone) (PVL) and P (ε-CL) have been documented (92-94). In 1996, Fritz's group (93) investigated the degradation behavior of PLA and PLA/PEG blends (PLA with 20 % PEG 400 and PLA with 20 % PEG 1500,

Table 3. Molecular weight values and PDI for the homopolymer formed from the Lipase CA catalyzed ring opening polymerization of 1,5-dioxepan-2-one (Uyama et al., 1995)

Product	M/In [a]	Mn [b]	Mn [c]	Mw [c]	PDI [c]	T_g [d] (°C)
1	30	7500	3400	13000	1.7	-40.6
2	55	9590	5200	20000	2.0	-39.5
3	100	15300	7400	33900	2.2	-38.4

[a]: Monomer to initiator ratio

[b]: Obtained by GPC with polystyrene standards

[c]: Determined by ^{1}H NMR

[d]: Obtained by DSC analysis

Table 4. Comparison of molecular weights and DPI of block copolyesters synthesized when aluminum isopropoxide ($Al(OiPr)_3$) was used as the catalyst (Lofgren et al., 1994)

Block copolyesters	Mn [a]	Mn [b]	DPI [b](Mw/Mn)
P(ε-CL) block	15500	8100	1.18
P(ε-CL)/P(DXO)	26500	8300	1.15
P(ε-CL)/P(DXO)/P(ε-CL)	31500	8100	1.18

[a]: Obtained by GPC with polystyrene standards

[b]: Determined by ^1H NMR

ε-CL: caprolactone

DOX: 1,5-dioxepan-2-one

PDI: polydispersity index

(respectively) with different molecular weight PEG. Thermal degradation of PLA and PLA/PEG blends can be described as follows: with 20 % PEG added to PLA, the degradation started at 50 °C, in comparison to the slightly slower degradation rate of PLA. This resulted from the plasticizing effect of PEG 400, which may increase the relative movement of the PLA chain at a lower temperature. When 20 % of the large molecular weight PEG 1500 was added to PLA, degradation started later than 50 °C. In this case, the plasticizing effect was probably not as pronounced and the degradation rate was even smaller (93).

In 2001, the effect of molecular weight on the thermal degradation of P(ε-CL) was studied by Dubois' (94) group using conventional and isothermal TGA, this is illustrated in Figure 7. The P(ε-CL) samples were submitted to a ramp of 20 °C/min under helium up to 600°C, and then under oxygen up to 800°C. It was found that lower molecular weight polymers decreased the thermal stability of the polymer chain faster than higher molecular weight polymers. The degradation step occurs at a much lower temperature, e. g. at 230 °C and 335 °C for P(ε-CL) 1800 and P(ε-CL) 42450. Such results can be explained by the pyrolysis rate of the polymer chain.

1.4 Summary

The following conclusions can be obtained from the literature review of this chapter:

1). Ozonolysis as a developed and economic process has been widely used to cleave carbon-carbon double bonds. Ketone, aldehyde, carboxylic acid and alcohol

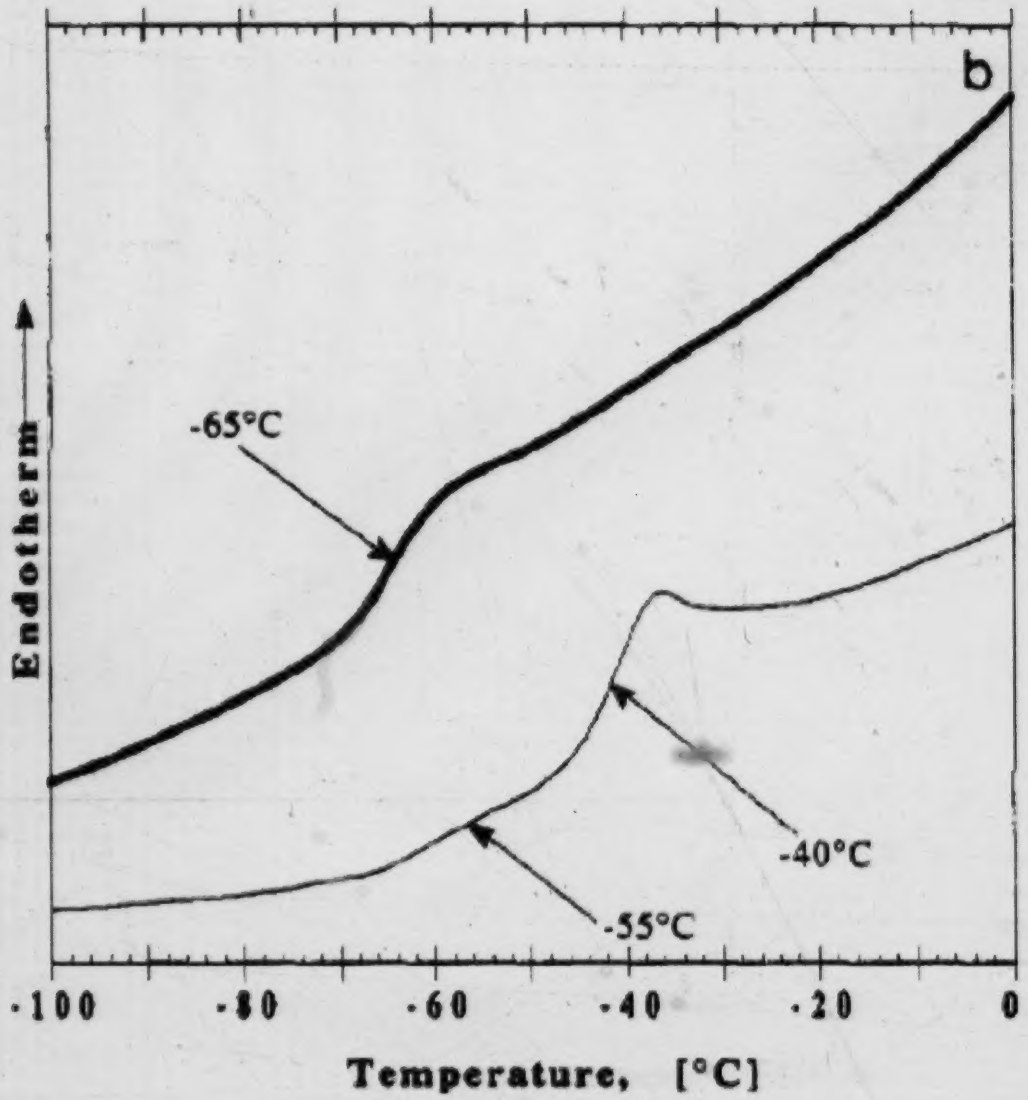


Figure 6: DSC thermogram of the Poly(ε-CL-b-DXO) copolymer (T_g of homopolymers of P(ε-CL) are shown on the upper curve, and the T_g of Poly(ε-CL-b-DXO) composed of 63 % P(ε-CL) is shown on the lower curve) (Lofgren et al., 1994)

intermediates can be synthesized via the stoichiometric or catalytic decomposition of ozonolysis intermediates.

2). Ozonolysis has also been applied on methyl esters of fatty acids, vegetable oils and their derivatives to produce advanced materials. Hydrogenation of ozonides can be performed under mild reaction conditions to form the corresponding alcohols.

3). Reported synthesis of nonanolactone was tedious and expensive, thus reliable and suitable process needs to be developed. As for the alternative monomer dilactone, its synthesis was not reported with high yield and purity.

4). Metal-containing catalysts, such as aluminium isopropoxide and lanthanum chloride, are commercially available chemicals and can be used as catalysts for ROP of lactones. Lipase catalysts are also efficient in catalyzing ROP; however, they are expensive and not suitable for scale up synthesis.

1.5 Overview of the starting materials and techniques employed

Polyester products that have been synthesized from raw materials derived from petrochemical reserves have been extensively studied and mass produced. The current depletion of these reserves has generated a need for a more renewable source. On the other hand, with the rising global use of fossil fuels comes an ever-increasing amount of greenhouse gas emissions, which result in a warmer atmosphere and global warming. Therefore, there is a need to develop new products and processes that are more environmentally friendly. Future products and processes need to be developed using a 'life cycle assessment' approach, where disposal or recyclability of the new

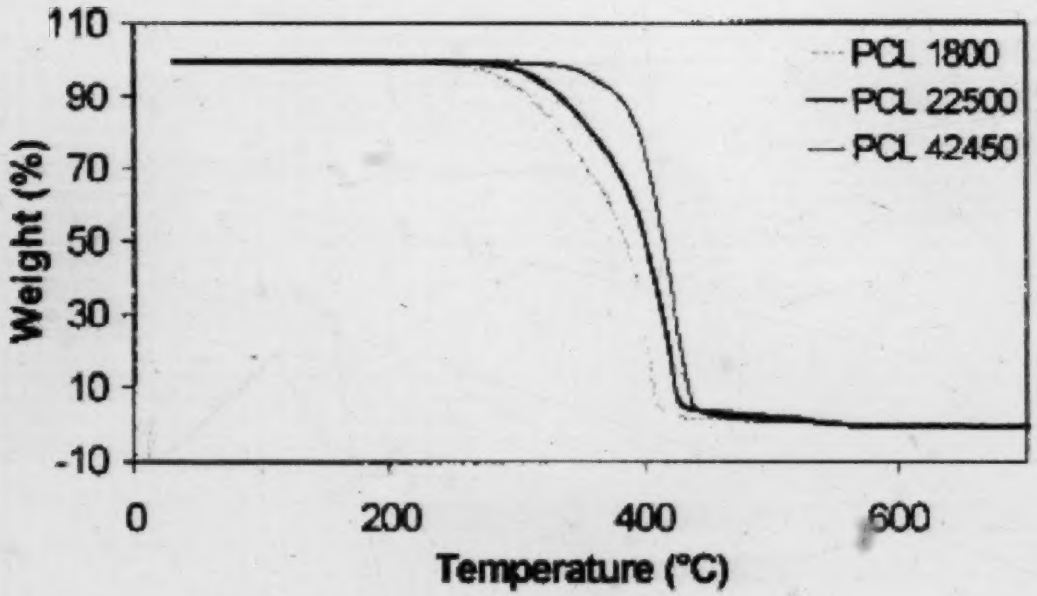


Figure 7: Conventional TGA thermocurves of PCL with different molecular weights

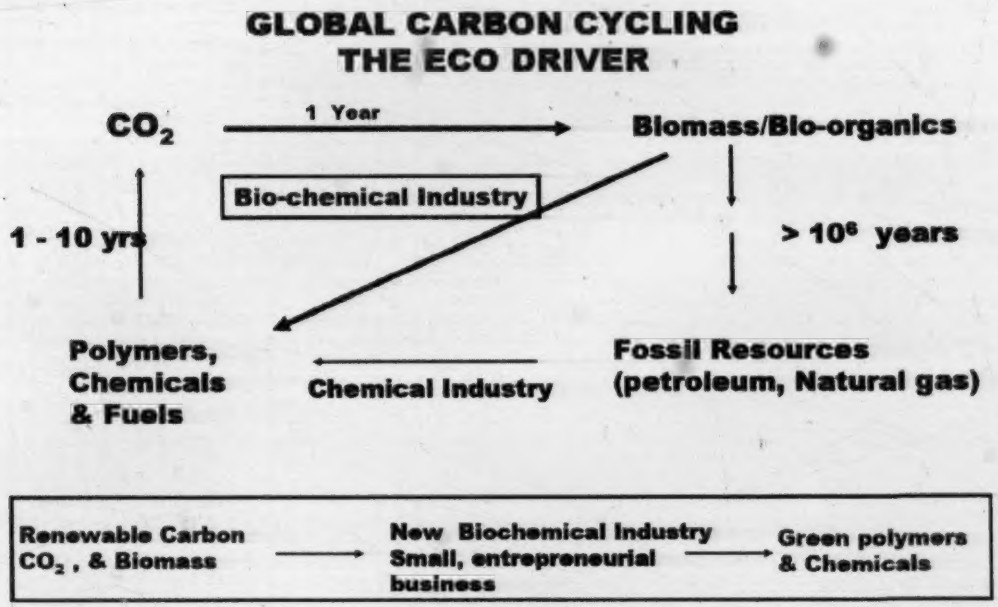
(Persenaire et al., 2001)

product needs to be taken into account in addition to the raw material source. From the global carbon cycle shown in Scheme 4 (Ramani Narayan, Michigan State University), it can be seen that current products derived from fossil resources require a long time before they are eventually recycled back into a usable source. If however, biomass or bioorganics can be utilized as a raw material source, this can initiate novel research in the biochemical industry for the production of 'green' polymers and materials. This will reduce the amount of time it will take for these new products to biodegrade and be recycled.

The diagram in Scheme 5 (Ramani Narayan, Michigan State University) shows how inorganic carbon can be converted into organic carbon through a photosynthetic process using autotrophs such as plants, algae and some bacteria.

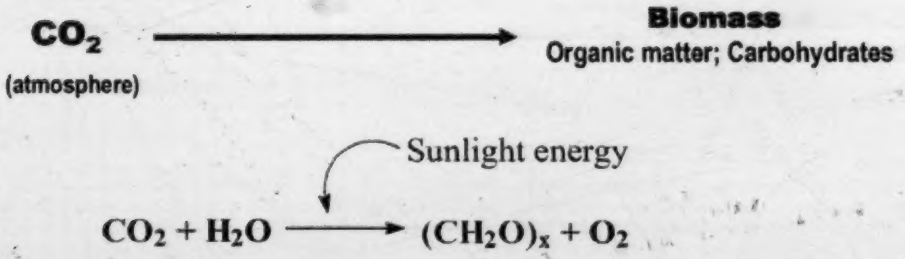
In order to produce environmentally friendly green polymers, it could be possible to use vegetable oil as the biomass starting material to develop novel polyesters that are anticipated to have comparable properties to those produced from petroleum resources. Considering the chemical content of vegetable oil, which contains many long chain unsaturated acids, it is feasible to produce 9-hydroxynonanoic acid, lactones or dilactones, which can be used as precursors for the formation of 'green' polyesters.

Vegetable oils in North America are largely made up of triacylglycerol (TAG) molecules. The fatty acids constituting most common North American seed oils predominantly have 0 to 3 double bonds, which provide the sites of reactivity to convert the TAG structure of the vegetable oil into a polyol (or other compounds). Polyols



Scheme 4: Global carbon cycling (Ramani Narayan, Michigan State University)

Inorganic to Organic carbon conversion



photoautotrophs -- algae, plants, and some bacteria fix inorganic carbon to **organic matter** (carbohydrates) using sunlight as the energy

Scheme 5: Inorganic to organic carbon conversion (Ramani Narayan, Michigan State University)

obtained from canola oil are one raw material that can potentially be used for the production of novel aliphatic polyesters. Canola oil which is under large scale production in Canada is a readily available, inexpensive and suitable material for this process. The general structure of a TAG in canola oil is shown in Figure 8. R could be: oleic acid, linoleic acid, linolenic acid, palmitic acid or stearic acid, as shown in Figure 9 and ester's structures are shown in Figure 10.

For the production of polyols from canola oils our group has developed a technology based on ozonolysis and hydrogenation reactions. (17, 95-98) These uncomplicated methods, as illustrated in Figure 11, are used to cleave the double bonds of fatty acids on the triglyceride backbone and to introduce functional groups to produce polyols.

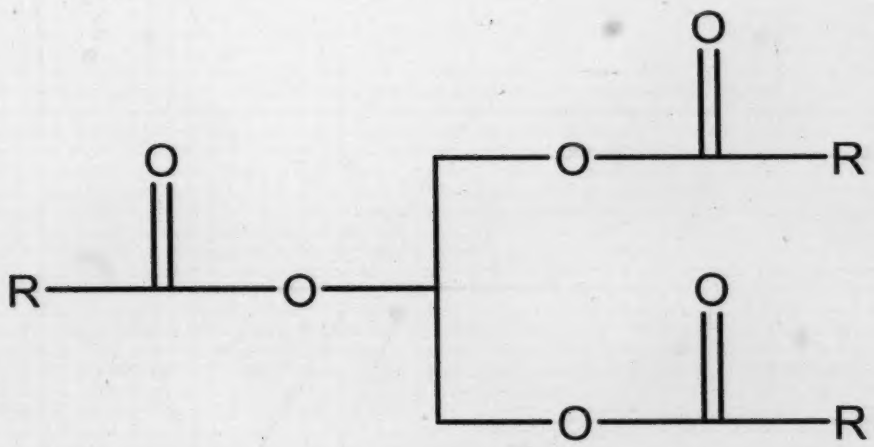


Figure 8: General structure of a TAG in Canola oil (Yue and Narine, 2007)

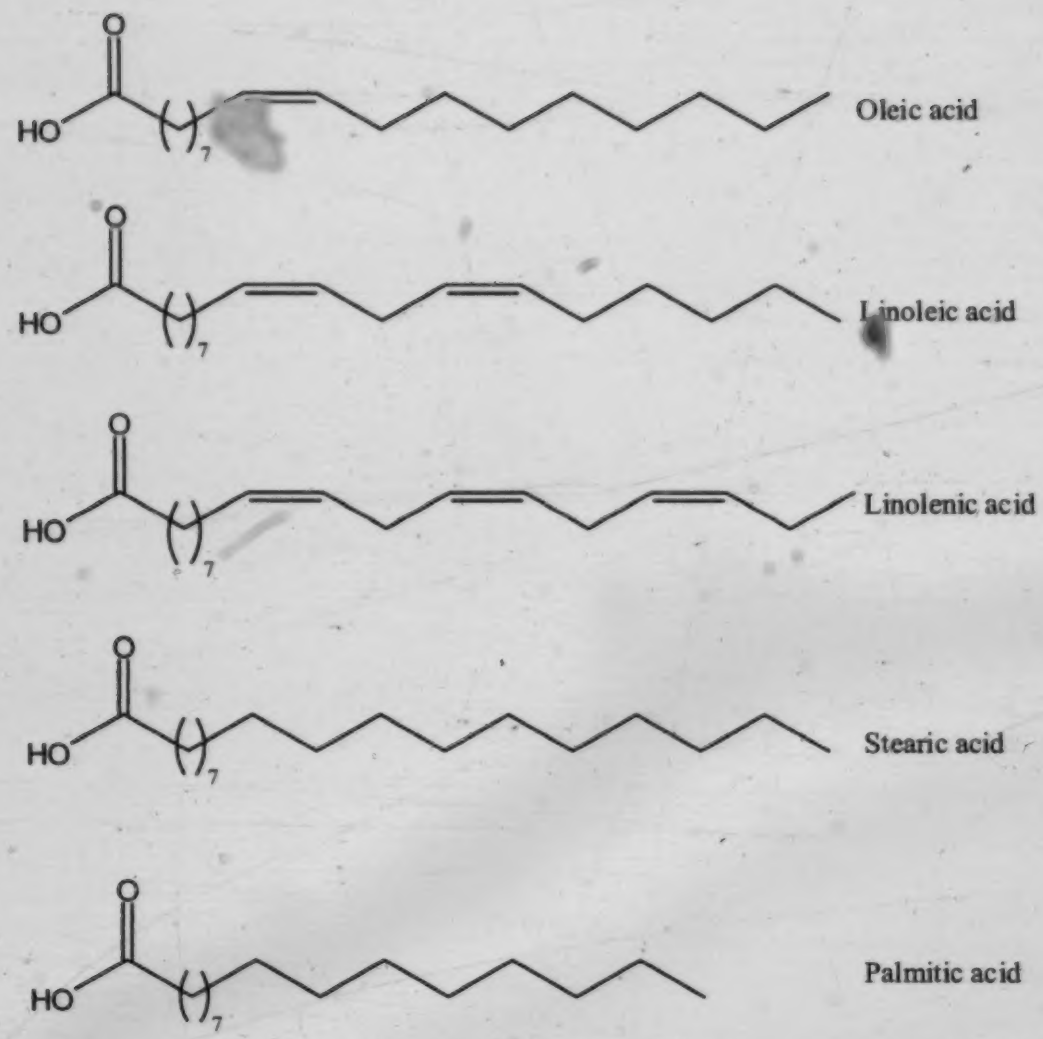


Figure 9: Main fatty acid components in the TAG backbone found in canola oil

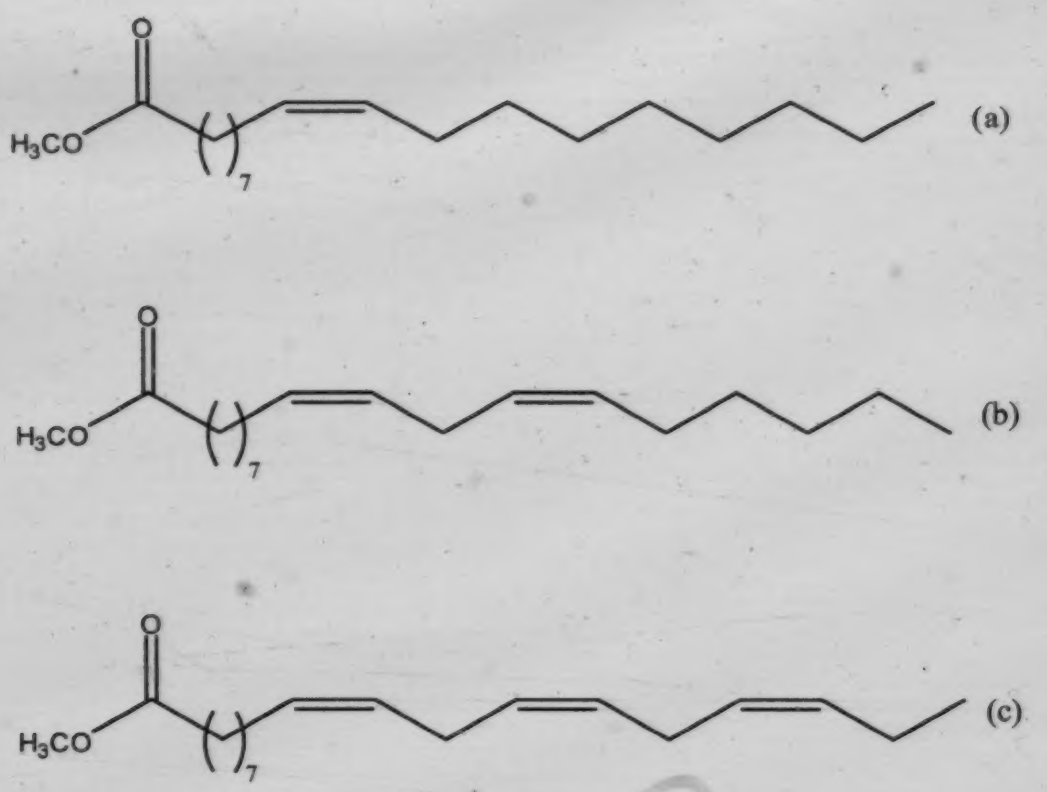


Figure 10: Ester mixtures of methyl oleate (a), methyl linoleate (b) and methyl linolenate (c)

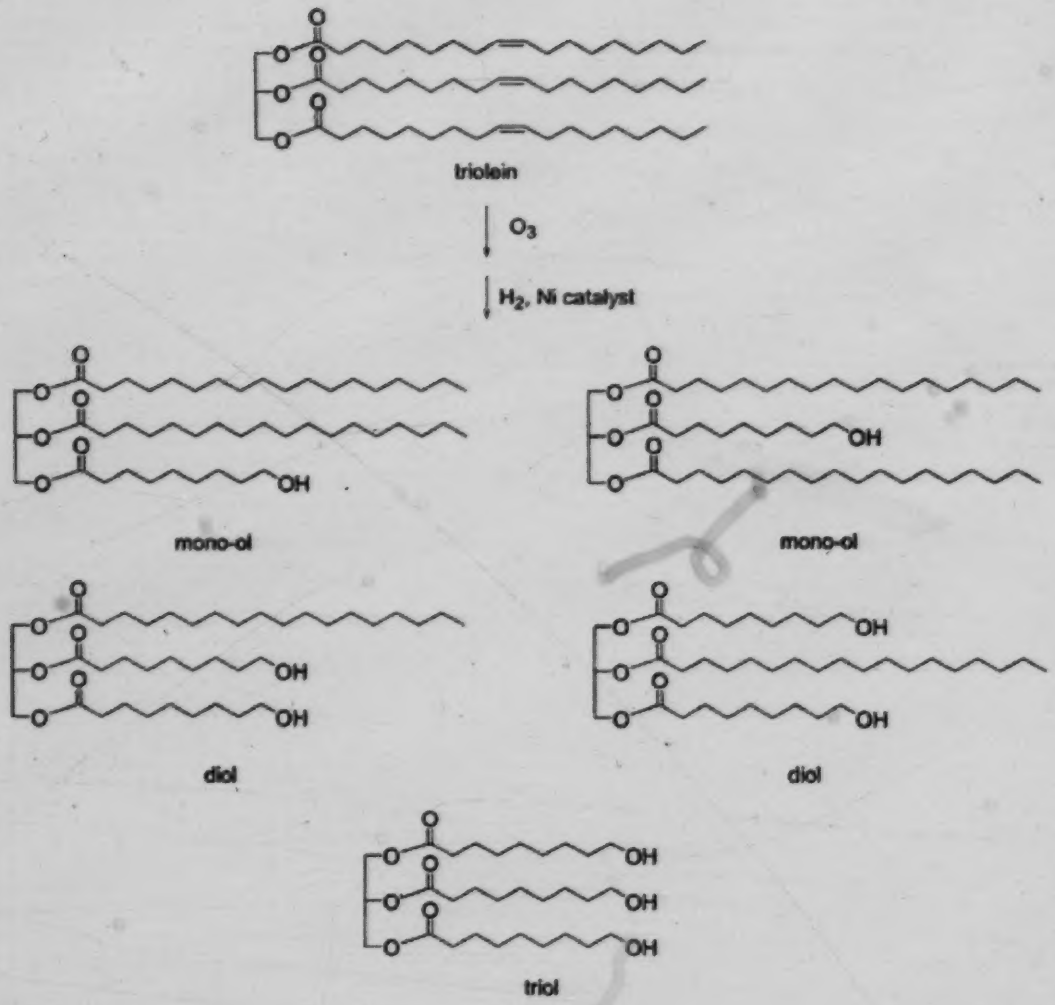


Figure 11: Production of polyols from triolein (Yue and Narine, 2006)

1.6 Aim and objective of the thesis

The concrete objectives of the research described in this thesis are to test the hypotheses stated below:

1). 9-Hydroxynonanoic acid may be synthesized using oleic acid, methyl oleate and polyol of Canola oil. The double bonds in the oleic acid and methyl oleate will be subjected to ozone, the ozonide will be hydrogenated to form alcohol under mild reaction conditions, and the ester group of methyl oleate will be saponified to obtain 9-hydroxynonanoic acid. 9-Hydroxynonanoic acid will also be obtained following saponification and acidification of polyol from canola oil.

2). Using 9-hydroxynonanoic acid as a reactant, other types of monomers, such as nonanolactone or dilactone, may be synthesized.

3). The monomer prepared in 2). may be used to synthesize polyester/polylactone.

Chapter 2 Experimental section

2.1 Synthesis and analytical methods

2.1.1 Preparation of 9-hydroxynonanoic acid

9-Hydroxynonanoic acid was prepared from three different starting materials: 1) oleic acid, 2) methyl oleate and 3) polyols of canola oil. All methods involved ozonolysis and hydrogenation techniques.

Materials

Oleic acid (90% purity), methanol, iodine, sodium thiosulfate and ethanol were purchased from Sigma-Aldrich, Chicago, USA. Methyl oleate was synthesized from oleic acid and methanol with catalytic amount of iodine. The polyols (95, 98) used in this Study was produced by our research group. from 100% pure canola oil supplied by Canbra Foods Limited, Lethbridge, AB, Canada. The Raney nickel 2800 (slurry in water), ethyl acetate and diethyl ether were obtained from Fisher Scientific Ltd. Canada. Silica gel (230-400 mesh) was obtained from Rose Scientific Ltd, AB, Canada. All the chemicals and solvents were reagent grade or better.

Equipment

Gas Chromatography (GC) System

A Varian 3500 Capillary GC equipped with a Flame Ionization Detector (GC-FID), Varian 8200 Auto Sampler and a BP20025 column (30m × 0.25mm i.d., 0.25-

μm) was used to identify and quantify the short chain compounds presenting as by-products of the

FTIR, NMR and Mass Spectrometry

FTIR spectra were measured with a Mattson Galaxy Series FT-IR 3000 spectrophotometer (Bio-Rad Microscience Ltd., USA). ^{1}H NMR and ^{13}C-NMR were recorded by 400 MHz and 100 MHz, respectively, using a Varian UNITY 400 (Varian, Inc., CA, USA), deuterated chloroform ($CDCl_3$) was used as solvent, and tetramethylsilane was used as an internal standard. Mass spectra were acquired on a Mariner Biospectrometry Workstation (PerSeptive Biosystems, Inc., MA, USA).

2.1.1.1 Synthesis of 9-hydroxynonanoic acid from oleic acid

Ozonolysis:

To a specially designed ozonolysis reactor (17, 99) (shown in Figure 12), 25.6 g of oleic acid and 700 ml of ethyl acetate were added. The reactor system incorporated a Direct Current Permanent Magnet and a HP Motor from Leeson electric-corporation, USA. Ozone was produced by an ozone generator (Azcozon Model RMV16-16 from Azco Industries Ltd, Canada). The reaction was performed at room temperature (approx. 20 °C), with a 5 L/min oxygen flow rate and 100 rpm agitation rate for 17 minutes. The concentration of ozone was 62.0 g/m^3 when oxygen is used as a feeding gas. After 17 minutes, the ozone generator was stopped and the reaction vessel was purged with nitrogen (N_2) for 3 minutes to remove any residue of ozone in the reactor vessel. To the ozonide product, 200 ml of ethyl acetate was added and the ozonide product was used for hydrogenation.

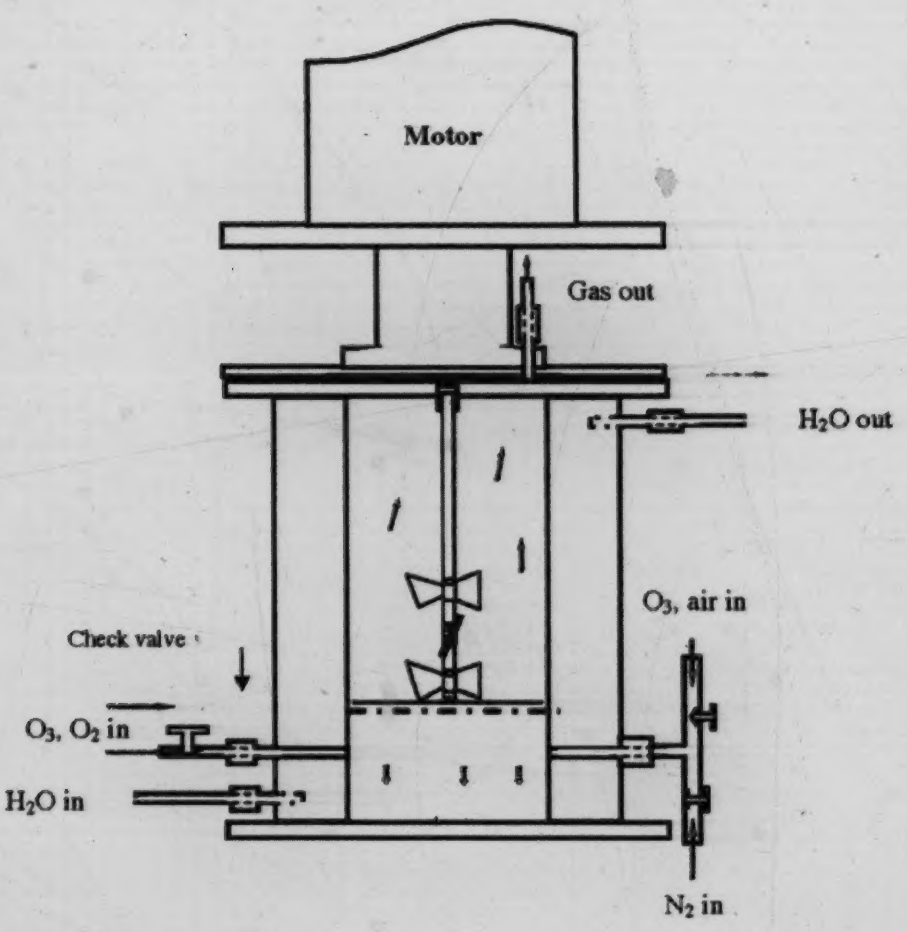


Figure 12: Schematic of the ozonolysis reaction vessel (Yue and Narine, 2006)

Hydrogenation:

5.0 g of Raney nickel catalyst (slurry in water) was added to the ozonide in a hydrogenation vessel (2 L, Parr Instrument Co, USA) fitted with a magnetic drive. The reaction vessel was charged with hydrogen gas at 100 psi and a temperature of 70 °C. After 3 hours, the hydrogen flow and heat were stopped and the temperature of the reaction vessel was allowed to cool to room temperature. The reaction vessel was then purged with nitrogen gas to remove any residue of hydrogen gas. The resulting mixture was filtered through a Buchner funnel. The filtrate was then transferred to a round bottom flask and solvent was removed by rotary evaporation. 14.2 g oily residue was obtained.

2.1.1.2 Synthesis of 9-hydroxynonanoic acid from methyl oleate

Preparation of methyl oleate:

Oleic acid (31.9 g, purity of 90%), methanol (100 ml) and iodine (319.0 mg) were added to a round bottom flask and the mixture was refluxed for 8 hrs. The progress of the reaction was monitored by TLC. After the reaction was complete, excess methanol was removed under reduced pressure and the residue was redissolved in diethyl ether (100 ml). The ether phase was washed with a solution of sodium thiosulfate aqueous solution (0.6 g, 50 ml) and then washed with brine (100 ml × 3), and finally dried over anhydrous sodium sulphate. The ether layer was concentrated under mild pressure to yield the crude product as yellowish oil (29.6 g and with a yield of 98 %) which was confirmed by ^{1}H NMR.

Ozonolysis:

To a 3-necked flask, 20.0 g of methyl oleate and 100 ml anhydrous ethanol were added. The flask was fed with a magnetic stirrer, inlet for ozone and outlet for gas. Ozone was produced by ozone generator (Azcozon Model RMV16-16 from Azco Industries Ltd, Canada) using cylinder oxygen as a feeding gas. The reaction was performed at -4 °C (ice-salt bath), at flow rate of 5 L/min of oxygen with an agitation rate of 100 rpm for 27 minutes. The concentration of ozone was 62.0 g/m^3. After 27 minutes, the ozone generator was stopped and the reaction vessel was purged with nitrogen (N_2) for 3 minutes to remove any residue of ozone in the reactor vessel. To the ozonide product, 800 ml of ethanol was added and the ozonide product was used for hydrogenation.

Hydrogenation:

5.0 g of Raney nickel catalyst (slurry in water) was added to the ozonolysis product in a hydrogenation vessel (2 L, Parr Instrument Co, USA) fitted with a magnetic drive. The reaction vessel was charged with hydrogen gas at 100 psi and a temperature of 70 °C. After 3 hours, the hydrogen flow and heat were stopped and the temperature of the reaction vessel was allowed to cool to room temperature. The reaction vessel was finally purged with nitrogen gas to remove any residue of hydrogen gas. The resulting mixture was filtered by Buchner funnel. The filtrate was then transferred to a flask and solvent was removed by rotary evaporation to yield 20.2 g of oily residue.

Hydrolysis:

The crude hydrogenated product (20.2 g) was reduced using 100 ml sodium hydroxide solution (8.0 %) for 3 hours. Afterward, the solution was cooled down to room temperature. The resulting mixture was then washed with ether (50 ml × 3). The combined ether layer was concentrated to give 7.2 g of n-nonanol (74 %). The aqueous layer was cooled down to 0 °C and acidified with concentrated hydrochloric acid (10.5 ml). The acidified mixture was extracted with ether (50 ml × 3). The organic layers were combined and washed with brine until neutral. The solution was finally dried with anhydrous sodium sulphate. Sodium sulphate was filtered off and the filtrate was concentrated with a rotary evaporator. Crude desired product was obtained as of a white solid (10.4 g). The product was further purified by recrystallization from diethyl ether to give 7.8 g of pure 9-hydroxynonanoic acid with a yield of 74%.

2.1.1.3 Synthesis of 9-hydroxynonanoic acid from polyols of canola oil

Hydrolysis:

The polyol mixture (30.2 g), sodium hydroxide (7.8 g) and 120 ml of distilled water were added to a 250 ml three-necked flask fitted with a condenser, magnetic stir bar and a thermometer. The reaction was refluxed (98 °C) for 2.5 hours, and then it was cooled to room temperature. The reaction mixture was extracted with ether (50 ml × 3) and the organic layers were combined and concentrated to give crude product 29.8 g of crude product. The crude product was then subjected to acidification.

Acidification:

The aqueous layer was added to a 250 ml flask with a stir bar and cooled in an ice bath for 10 minutes. Concentrated hydrochloric acid (36.5%) was added gradually at 0 °C until the solution was at pH value of the solution was about 2 (as measured using a pH meter). The acidic mixture was then extracted with ether (50 ml × 3). The organic layers were combined and washed with brine (100 ml × 3) until the solution became neutral. The solvent was removed by rotary evaporation to yield the crude product as a viscous oily residue. After standing at room temperature overnight, the residue became a pale yellow solid. The crude product was recrystallized from acetone to yield two components, labelled A and B. The filtrate was concentrated to yield 21.5 g of a pale yellow solid.

Flash Chromatography:

1.3 g of the pale yellow solid (obtained from concentration of the filtrate) was purified by silica flash chromatography using a column with the dimensions 3 cm × 30 cm and packed with 230 - 400 mesh silica gel. The column was eluted with a gradient flow phase composed of hexane and ethyl acetate (Ethyl acetate : Hexanes = 1:10, 1:5 to 1:3). Thin layer chromatography (TLC) plates were stained with phosphomolybdic acid.

After separation, fractions C and D were acquired, and component C was obtained as the main product. The four fractions A, B, C and D were submitted to GC-FID, NMR and HR-MS. Fractions A and B were confirmed to be palmitic and stearic acid by GC-FID with corresponding steric acid and palmitic acid standards. Component D was ester mixtures and component C was identified to be 9-hydroxynonanoic acid.

2.1.2 Preparation of nonaonolactone and dilactone

Materials

9-hydroxynonanoic acid (98 % purity) was synthesized from methyl oleate. Concentrated hydrochloric acid (36.5%), boron trifluoride in methanol (13% BF_3 dissolved in methanol), *p*-toluenesulfonic acid and N, N'-Dicyclohexylcarbonyldiimide (DCC, 98%), Anhydrous tetrahydrofuran (THF), toluene and xylene as well as 3Å molecular sieves (which were activated at 300 °C for 3 hours before use) were purchased from Sigma-Aldrich, Chicago, USA. Hafnium chloride (98% pure, 1-3 % Zr) was purchased from Alfa Aesar, Maryland, USA. All the solvents used were ACS grade or better.

Equipment

Gas Chromatography Mass Spectroscopy Detector System

An Agilent technology 6890 Capillary GC equipped with a 5975B inert XL Mass Spectroscopy Detector (GC-MSD) with a molecular ion range of 1000 was used for analysis. Agilent technologies 7683 B series Auto Sampler Injector that can inject 1.0 μL sample with a split ratio of 80:1 and an HP-5 column (30m × 0.25mm, i.d., 0.25-μm) was used to identify the lactone products. The temperature of the column was initially set at 70 °C and held for 0.5 minutes, then the temperature was set to increase to 250 °C at a rate of 10 °C/min and the temperature was held for 20 minutes.

2.1.2.1 Preparation of monolactone via melt condensation reaction

9-hydroxynonanoic acid (5.0 g) was added to a three neck flask fitted with a magnetic stir bar and connected to a high vacuum oil pump (<0.35 Torr). The flask was heated to 220 °C (monitored by thermometer) and the reaction proceeded for 2 hours. Following this, the vacuum was removed and the reactor was cooled down to room temperature and 4.8 g of a yellow powder was obtained.

2.1.2.2 Attempt to prepare nonanolactone using different catalysts

To a three necked flask, 217.0 mg of 9-hydroxynonanoic acid and 8 ml of CH_2Cl_2 were added. DCC (257.0 mg) was dissolved in 2 ml of CH_2Cl_2 and the solution was added to the above flask dropwise. The reaction mixture was stirred at room temperature for 12 hours. The solvent was removed by rotary evaporator, and then 10 ml of ethyl acetate was added. Precipitation was filtered off and the filtrate was concentrated again. Repeating the dissolve-filtering procedure for 2 more times, the final filtrate was concentrated and 212.0 mg of residue was obtained.

9-hydroxynonanoic acid was used as a starting material and an attempt made to synthesize nonanolactone catalyzed by 20 mol % of HCl (Conc: 36.5 %); 50 mol % of HCl; 20 mol % of *p*-toluenesulfonic acid; and 20 mol% of BF_3-CH_3OH respectively. Unfortunately, no nonanolactone was found, chain ester mixtures were obtained instead (the molecular weight of the chain ester mixtures obtained were 344, 500, 656, and 812). Among them, more than 90% chain ester with molecular weight of 344, the other 10% are chain esters with molecular weight from 500 to 812.

2.1.2.3 Preparation of dilactone from 9-hydroxynonanoic acid

A dried 25 ml three necked flask was equipped with a Teflon-coated magnetic stir bar, a 15 ml pressure equalized addition funnel (containing a cotton plug and molecular sieves 3Å (6.0 g)) and a reflux condenser. 9-hydroxynonanoic acid (5.0 g, 28.6 mmol), $HfCl_4$ (225.0 mg, 0.7 mmol) and 10 ml of xylene were added to the flask. After 24 hours of refluxing, the resulting mixture was cooled to ambient temperature and dissolved in 8 ml chloroform. Acetone was added to precipitate the product which was obtained as a yellowish powder in almost quantitative yield (98 %).

2.1.3 Synthesis of polyesters / polylactones

Materials

Dilactone (purity of 98%) was synthesized from 9-hydroxynonanoic acid catalyzed by hafnium chloride. Aluminium isopropoxide (99%) and lanthanum chloride (99%), Lipase CA, THF, Toluene and DCM were purchased from Sigma-Aldrich Chicago., USA. All the solvents were ACS grade or better.

Molecular Weight Measurements by GPC and ^1H NMR

The number- and weight- average molecular weights (Mn and Mw, respectively) were determined by gel permeation chromatography (GPC). Studies by GPC were carried out using an Agilent G1311A quat pump, G1362A refractive index detector and a PL gel column (5μm mixed-D). Chloroform was used as the eluent at a flow rate of 1.0 mL/min. Sample concentrations of 0.4% (w/v) and injection volumes of 10 μl were used. Polystyrene standards were used to generate a calibration curve.

Molecular weights of polyesters were also measured by end group analysis with ^{1}H-NMR. The progress of polymerization of the hydroxylesters was followed by the steady increase of the signal intensity of the two end groups: the iso-propyl group adjacent to the ester functionality and the methylene group adjacent to the hydroxyl group.

Modulated Differential Scanning Calorimetry (MDSC)

The "TA 2920 Modulated DSC" system from TA Instruments was used to analyze the thermal behaviour of the polyester. The procedure to record the crystallization and melting curves was as follows: Initially the sample was kept at 20 °C for 3 min to reach its equilibrium state and then was heated to 120 °C at a rate of 20 °C/min to erase its thermal history. To record the crystallization curve, the sample was cooled down to -60 °C at a constant rate of 5 °C/min and kept at this temperature for 3 min to allow for the completion of the crystallization. The sample was then heated to 120 °C at a constant rate of 10 °C/min to record the melting curve.

The relative crystallinity of the polyesters was calculated according to the following equation:

$$w_c = \frac{\Delta H_f}{\Delta H_f^\circ} \times 100 \qquad \text{Equation (2)}$$

Where w_c is the relative crystallinity, ΔH_f is the heat fusion of the polyesters, ΔH_f° is the heat of fusion of 100% crystalline polyester, which was 204.5 J/g. (100)

Thermogravimetric Analysis (TGA)

TGA was carried out on a TGA Q50 Thermogravimetric Analyzer (TA Instruments, UK) following the ASTM D3850-94 standard. The sample was ground to a powder and approximately 10 mg of the specimen was loaded into an open platinum pan which was pre-flamed. The samples were heated from 25 °C to 600 °C under dry nitrogen at a constant heating rate of 10 °C/min.

2.1.3.1 ROP of dilactone catalyzed by lanthanum chloride

A three necked round bottom flask, previously flamed and purged with dry nitrogen three times, was fixed with a condenser with a dry nitrogen inlet. The dilactone monomer (522.0 mg, 1.7 mmol), $LaCl_3$ (6.1 mg, 0.3 mmol) and 10 ml dry toluene were added to the flask. The reaction was refluxed for 24 hrs under a nitrogen atmosphere. The reaction was then cooled to room temperature and the reaction mixture dissolved in $CHCl_3$. Polymer was precipitated with excess methanol. After washing with methanol several times and drying under vacuum, 0.3 g of a solid was obtained.

2.1.3.2 ROP of dilactone catalyzed by aluminium isopropoxide

To a flame dried round bottom flask, $Al(O\textit{i}\text{-}Pr)_3$ (19.0 mg, 0.1 mmol) and dilactone (1.0 g) was added under a nitrogen atmosphere. Dry toluene 10 ml was then added through a rubber septum using a syringe. After 24 hours at 80°C, the polymerization reaction was stopped by adding a 3-fold molar excess of 0.5 M HCl. Initiator residues were removed by two successive extractions with an aqueous solution of 0.1 M EDTA, followed by repeated washing of the organic phase with water. The

polymer was recovered by precipitation in methanol and was dried under reduced pressure at room temperature until no change in weight was observed and 0.4 g of solid was obtained.

2.1.3.3 ROP of dilactone catalyzed by lipase CA

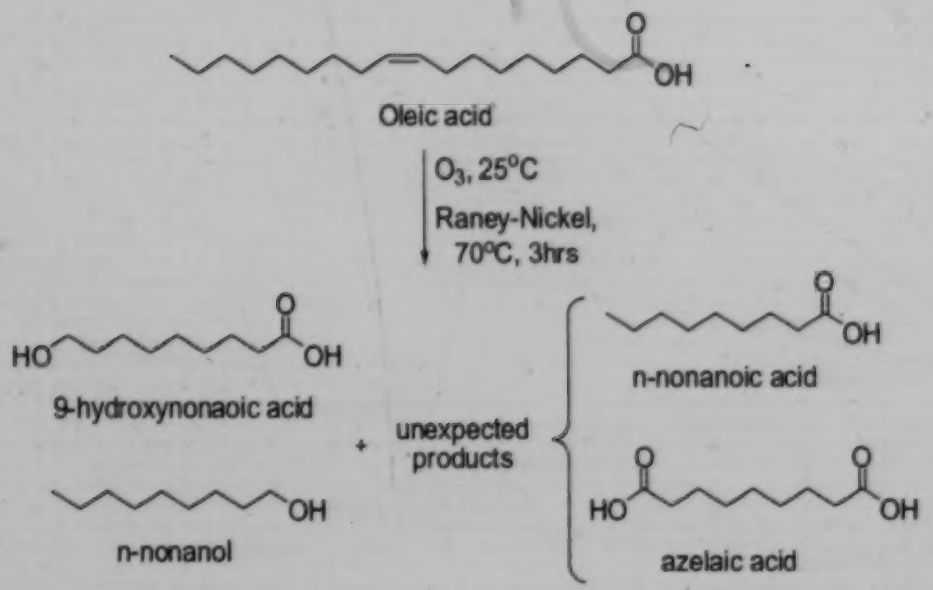
To a flame dried round bottom one neck flask, 312 mg (1.0 mmol) of dilactone, 0.1 g of lipase CA and isooctane (5 ml) were added. The flask was sealed and kept under gentle stirring at 80 °C for 240 hours. After evaporation of the solvent under reduced pressure, the residue was extracted with chloroform and lipase CA was separated out by filtration. The filtrate was concentrated and precipitated in methanol. The polymer was isolated by re-precipitation and 95 mg of a solid was obtained.

Chapter 3 Results and discussion

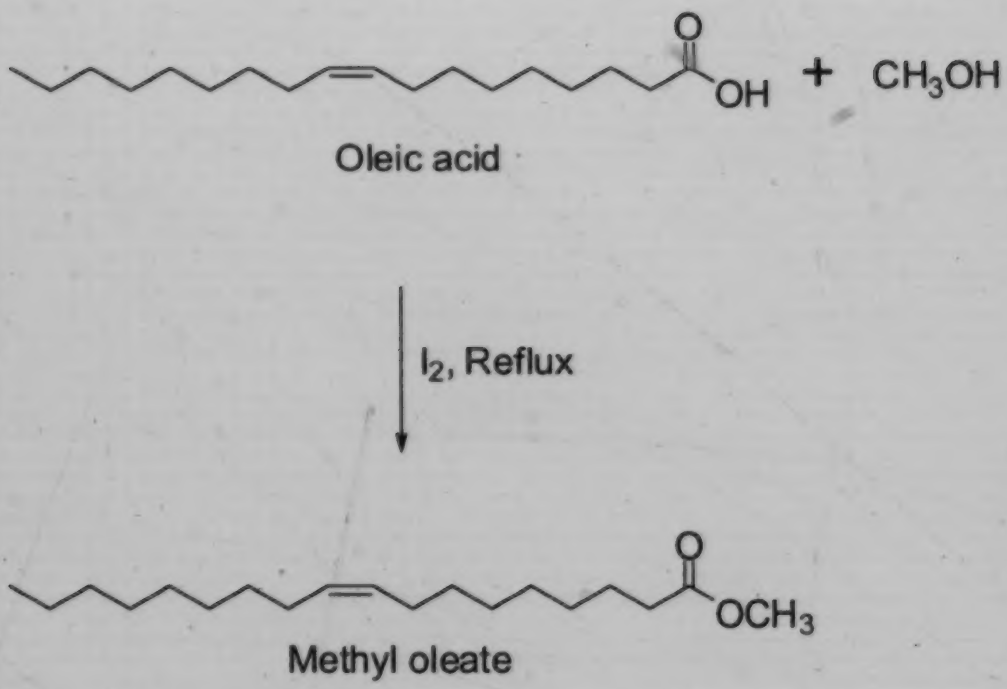
3.1 9-Hydroxynonanoic acid obtained from oleic acid

9-hydroxynonanoic acid can be produced *via* a tandem ozonolysis and hydrogenation reaction on oleic acid (11). However, it was discovered that in addition to the desired product 9-hydroxynonanoic acid, by-products of n-nonanoic acid and azelaic acid were also obtained, which are shown in Scheme 6. The molar ratio of products of 9-hydroxynonanoic acid to azelaic acid to n-nonanoic acid was found to be 1:1.5:1. A perceptible rise in temperature during the ozonolysis was discernible. This could be due to the ozonolysis reaction being carried out at room temperature (approx. 20 °C) and the heat produced during the exothermal reaction not being able to be dissipated immediately, leading to an increased reaction temperature resulting in the possibility of intermediates being further oxidized to acids. The carboxylic group was not compatible; it may have interaction with ozonide and as a result, the by product acids were found. According to the molar ratio estimated by integration of corresponding peaks in the ^{1}H NMR, the yield of 9-hydroxynonanoic acid is approximately 28 %, indicating that this is not feasible for the large scale synthesis.

In an attempt to produce 9-hydroxynonanoic acid with high purity, oleic acid was converted to the intermediate, methyl oleate, *via* the reaction of oleic acid with methanol in the presence of catalytic iodine, as shown in Scheme 7.



Scheme 6: Synthesis of 9-hydroxynonaoic acid from ozonolysis and reduction of oleic acid



Scheme 7: Synthesis of methyl oleate (FAME) from oleic acid, catalytic iodine and methanol.

3.2 9-Hydroxynonanoic acid obtained from methyl oleate

Using methyl oleate as a starting material, a procedure involving ozonolysis, hydrogenation, hydrolysis and acidification was carried out to produce crude 9-hydroxynonanoic acid (3). The crude product was first submitted for GC-FID analysis with a BP-20 column. According to the GC-FID chromatogram, the crude product contained 2 components. It was found that one component was n-nonanoic acid (a signal peak having a retention time of 16.0 minutes), and the other component was 9-hydroxynonanoic acid (a signal peak with a retention time of 23.1 minutes). These were compared to the retention times of standard samples of n-nonanoic acid and 9-hydroxynonanoic acid and showed a tolerance of less than 1 %. In order to obtain high purity of 9-hydroxynonanoic acid, the crude product was recrystallized from diethyl ether and the purity (as analyzed by ^{1}H NMR) was found to be 98 %.

As can be seen from Table 5, 9-hydroxynonanoic acid was synthesized from methyl oleate with yield 74 % following a five step reaction. In addition, n-nonanol, a by-product of the process and an expensive solvent, was obtained in high purity (98 %) with the yield of 82 %. Using this procedure, three batches of reactions were carried out to investigate the reproducibility of the reaction. According to the results obtained in these three batches, as shown in Table 5, this process is reproducible with high yield and high purity. This methodology was also amenable for the production of 9-hydroxynonanoic acid on a larger scale using 100 g of starting material.

Table 5. Reproducibility of the synthesis of 9-hydroxynonanoic acid from methyl oleate

Entry No.	methyl oleate (g)	9-hydroxynonanoic acid (Mass)		n-nonanol (Mass)	
		g [a]	Yield [b]	g [a]	Yield [b]
1	20.02	6.55	70%	7.21	74%
2	44.20	16.76	72%	17.67	81%
3	100.02	44.86	74%	44.64	91%
Average			72%		82%

a: Obtained by mass.

b: Yields are as a percentage of theoretical yield.

Recrystallized 9-hydroxynonanoic acid was submitted for ^{1}H NMR, ^{13}C NMR and HR-MS analysis for structural confirmation.

The high resolution mass spectroscopy (HR-MS) analysis obtained using negative mode electron spray ionization showed that the molecular ion, 173.1171, corresponded to $[C_9H_{17}O_3]^-$. The high resolution mass spectrum is shown in Figure 13.

The recrystallized 9-hydroxynonanoic acid was also analyzed by FTIR as shown in Figure 14. The FTIR spectrum shows a characteristic absorption band for the hydroxyl group (-OH) centered at 3334 cm^{-1} and absorption bands for the asymmetrical and symmetrical vibrations of the methylene groups centered at 2931 cm^{-1} and 2852 cm^{-1} respectively. The absorption band for the carbonyl group (C=O) occurs at 1693 cm^{-1}.

The ^{1}H NMR spectrum of the crystallized acid is shown in Figure 15. The broad signal at approximately 5.0-7.0 ppm corresponds to the proton of hydroxyl group (-OH). Due to the electron withdrawing effect of the hydroxyl group, the methylene protons adjacent to the –OH group occur at 3.65 ppm. The methylene protons adjacent to the carbonyl group (C=O) occur at 2.35 ppm. Two sets of multiplets occur between 1.50 ppm and 1.70 ppm, these correspond to the two methylene groups, -$C\underline{H}_2CH_2COOH$ and -$C\underline{H}_2CH_2OH$. A broad absorption occurring between 1.25 ppm and 1.30 ppm corresponds to the four methylene groups (-$CH_2CH_2CH_2CH_2$-) located in the middle of the hydroxyl fatty acid chain.

The ^{13}C NMR spectrum of pure 9-hydroxynonanoic acid is shown in Figure 16. The signal at 179.36 ppm is indicative of the carbon of the carboxylic acid functionality and the signal at 62.94 ppm corresponds to the carbon adjacent to the hydroxyl group.

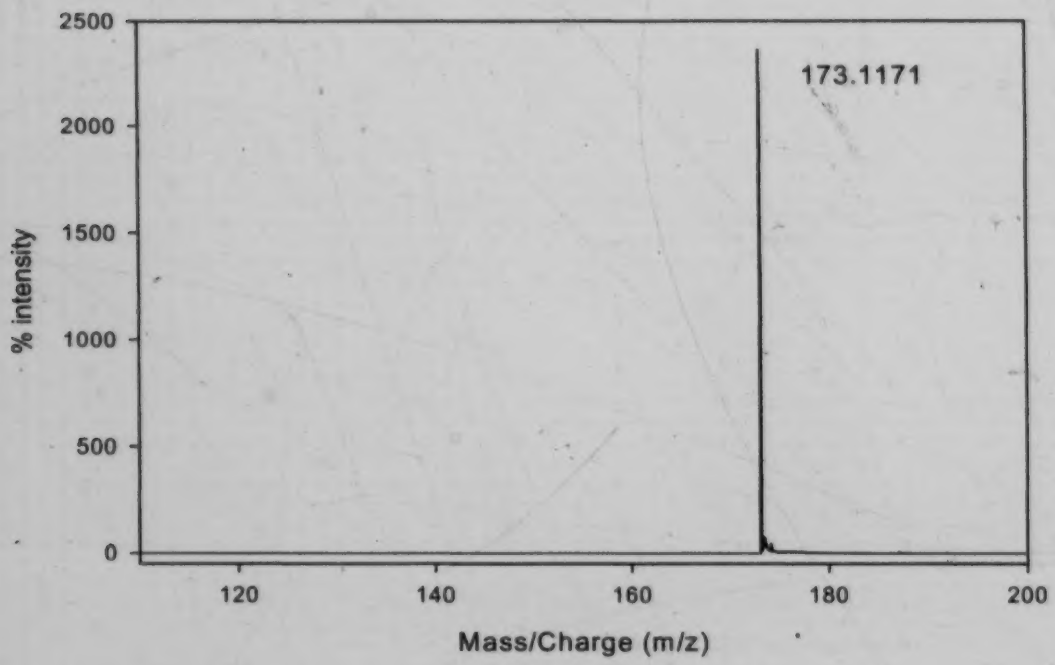


Figure 13: High resolution mass spectrum of 9-hydroxynonanoic acid

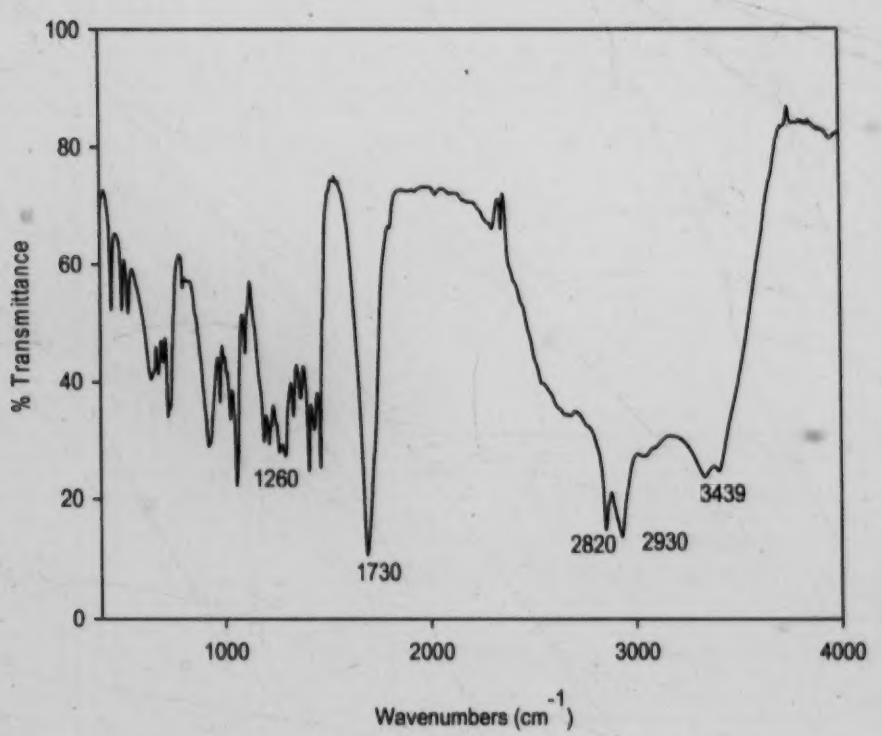


Figure 14: FTIR spectrum of 9-hydroxynonanoic acid

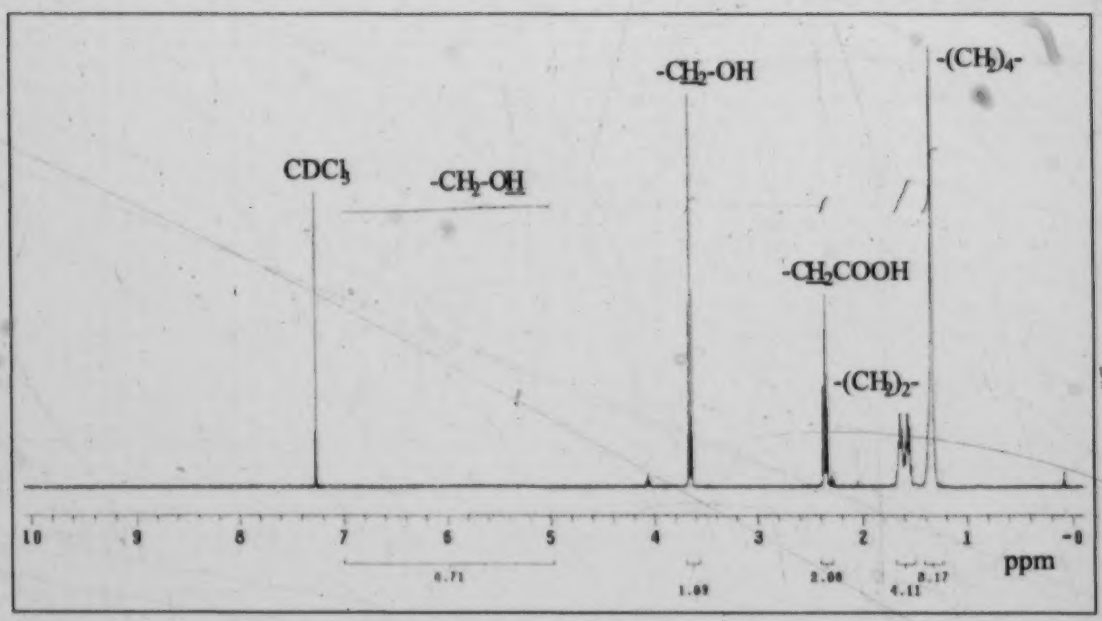


Figure 15: ^{1}H NMR spectrum of 9-hydroxynonanoic acid

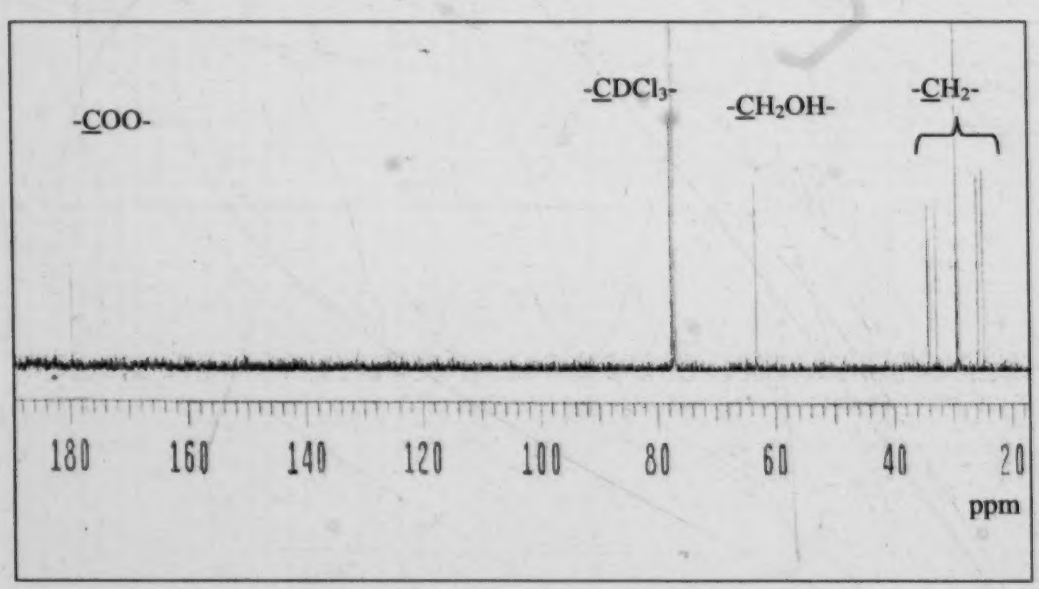


Figure 16: ^{13}C NMR spectrum of 9-hydroxynonanoic acid

The chemical shifts at 33.97, 32.59, 29.11, 28.91, 25.59, 24.63 ppm are due to the remaining alkyl carbons.

Information obtained from HR-MS, FTIR, ^{1}H NMR, and ^{13}C NMR confirmed the structure of the product obtained after recrystallization to be 9-hydroxynonanoic acid, and here is a spectra data summary of 9-hydroxynonanoic acid: *HR-MS*: (ESI) *m/z* observed: 173.11711 ($[M-H]^-$), calculated: 173.12045; *FTIR:* 3334 cm^{-1}, 2931 cm^{-1}, 2852 cm^{-1}, 1692 cm^{-1}; *^{1}H-NMR* ($CDCl_3$ 400 MHz): δ 2.35 (m, 2 H, -C<u>H</u>$_2$COOH), 3.65 (t, J = 7.0 Hz, -C<u>H</u>$_2$OH), 1.65 (m, 2 H, -C<u>H</u>$_2$CH$_2$OH), 1.55 (m, 2 H, -C<u>H</u>$_2$CH$_2$COOH), 1.35 (s, 8 H, -C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$-), 5.0~7.0 (bs, 2 H, average of -CH$_2$COO<u>H</u> and -CH$_2$O<u>H</u>); *^{13}C-NMR* ($CDCl_3$ 100 MHz): δ 173.36 (-<u>C</u>OOH), 62.94 (-<u>C</u>H$_2$OH), 33.97, 32.59, 29.11, 29.12, 28.91, 25.59, 24.63.

The effect of solvent was also examined in the reaction involving methyl oleate as the starting material. Reactions were carried out in both ethanol and ethyl acetate and the yields and purity of the products were compared. It was found that, of the two solvents, ethanol gave the product in higher yield and purity. This could be due to the fact that ethanol is a protonic solvent and therefore has a stronger ability (in comparison to ethyl acetate) to trap the ozonide formed in the ozonolysis reaction. The mechanism for the ozonolysis reaction is shown in Figure 17 and Figure 18. The protonic solvent trapped the ozonide and avoided over oxidation of ozonide, and as a result, 9-hydroxynonanoic acid obtained from using ethanol as a solvent is purer in comparison to that obtained from using ethyl acetate as a solvent. The yield and purity results are shown in Table 6.

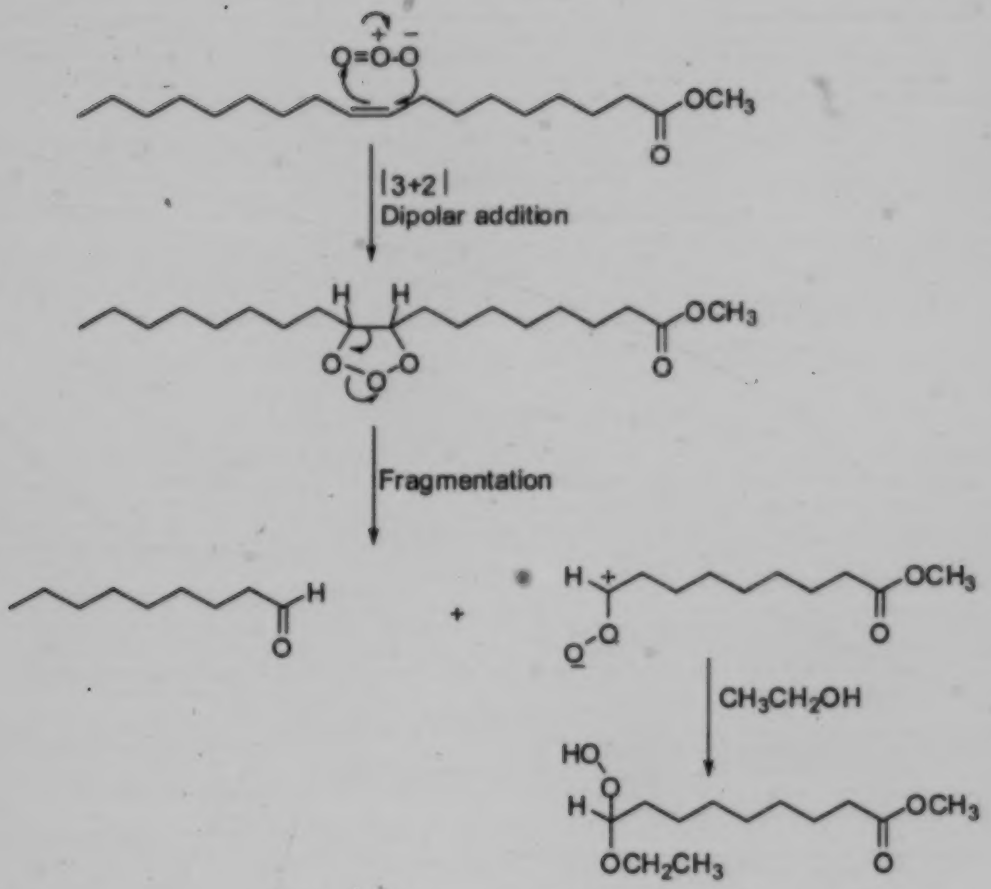


Figure 17: Mechanism for the ozonolysis of methyl oleate

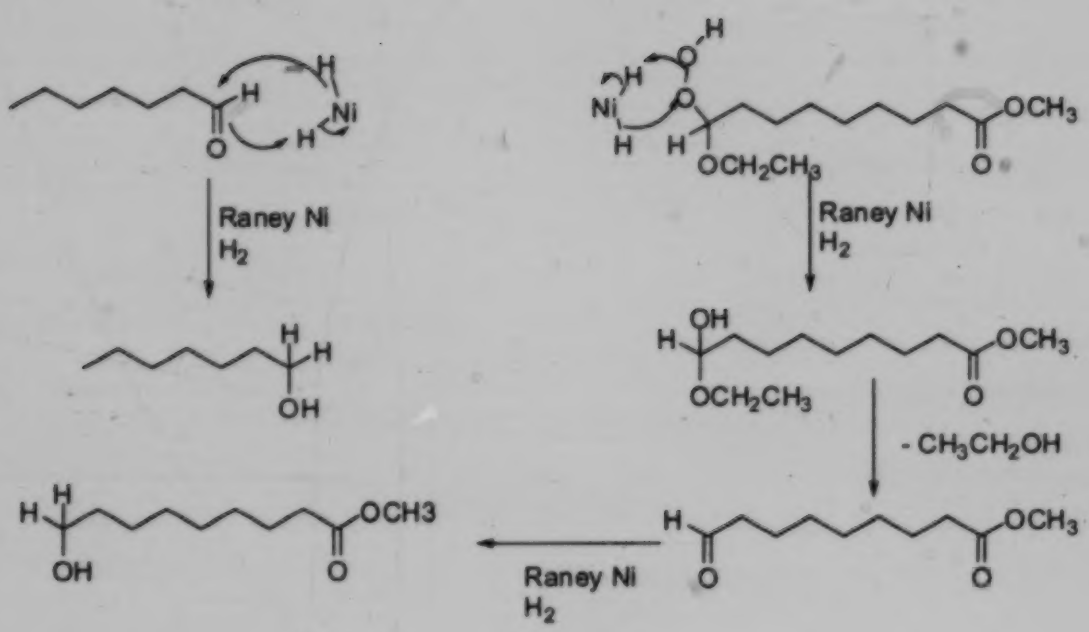


Figure 18: Mechanism for hydrogenation of the ozonide intermediates

Table 6. Synthesis of 9-hydroxynonanoic acid using different solvent systems and comparison of product purity

Starting material [a] (g)	Solvent	Yield [b] (%)	Purity [c] (%)
20.02	Ethyl acetate	Not calculated	50
20.02	Ethanol	74	98

[a]: Starting material is methyl oleate

[b]: Yields are as a percentage of theoretical yield

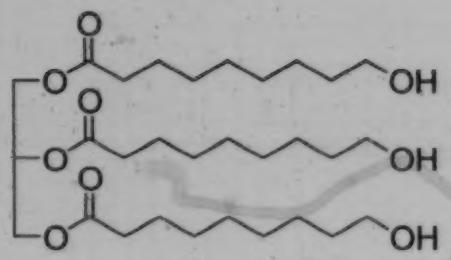
[c]: Calculated by ^{1}H NMR.

3.3 9-Hydroxynonanoic acid obtained from polyols of canola oil

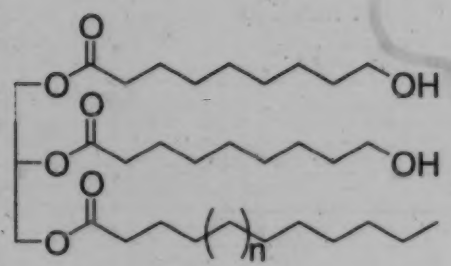
Polyol of canola oil is composed of triol, diol and mono-ol, and its main compositions (95) are shown in Figure 19. After hydrolysis of the polyol and then acidification, the crude products were obtained. These were purified by recrystallization and then by flash chromatography, 4 different fractions (A, B, C and D) were obtained.

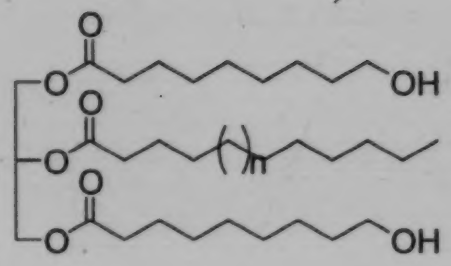
Components A and B obtained from the recrystallization step with acetone were identified as palmitic acid and stearic acid, respectively. These components were analyzed by GC-FID and the results compared with the retention times of standards and showed a tolerance of less than 1.0 %. Fractions C and D that were obtained following separation by flash chromatography were submitted to HR-MS, FTIR and NMR analysis. Fraction C was identified as 9-hydroxynonanoic acid, which was the main product of the reaction and fraction D was identified as a mixture of lactone, dilactone and chain esters. Fraction D could be a result of inter- and intra-molecular condensation reactions of the product during the solvent concentration process.

To the best of our knowledge, this is the first time that 9-hydroxynonanoic acid has been produced from polyols obtained from commercial canola oil. According to the results shown in Table 7, the yields of 9-hydroxynonanoic acid produced from different batches of polyols show that the reaction is reproducible.

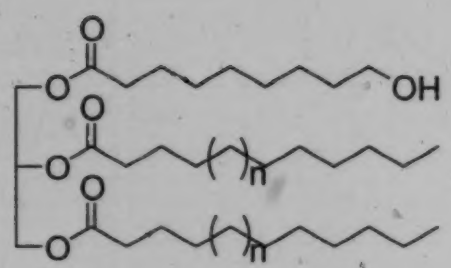


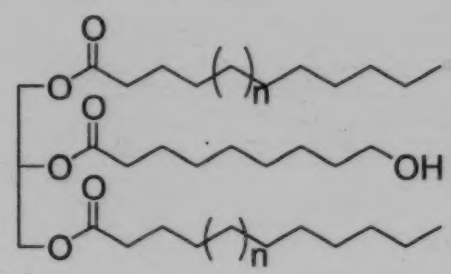
Triol





Diol (n= 6 or 8)





Mono-ol (n= 6 or 8)

Figure 19: Polyols composition of canola oil

Table 7. Reproducibility of the reaction to produce 9-hydroxynonnanoic acid from polyol of canola oil

Entry No.	Polyol [a] (g)	Palmitc and stearic acid (g)	Crude 9-hydroxynonanoic (g)	Yield [b] of 9-hydroxynonanoic acid
1	10.06	0.63	7.44	57 %
2	30.10	2.67	22.20	56 %
3	30.12	1.94	22.50	58 %

[a]: Polyol of canola oil.

[b]: Pure 9-hydroxynonanoic acid separated by flash column chromatography and . yields are as a percentage of theoretical yield

3.4 Synthesis of lactone and dilactone

3.4.1 Using melt condensation reactions

Six different reaction conditions were tried for the melt condensation of 9-hydroxynonanoic acid. The temperature was varied from 96 °C to 230 °C, the pressure was changed from 30 Torr to 0.35 Torr and the reaction time was set at either 2 or 4 hours. The results are shown in Table 8. The obtained melt condensation product was a mixture of chain esters, unfortunately, no desired lactone was observed.

According to the data obtained from the different reaction batches listed in Table 8, the higher the temperature and the lower the pressure, the higher the conversion of 9-hydroxynonanoic acid. At 96 °C, the reaction catalyzed with HCl has a higher conversion to 9-hydroxynonanoic acid than the reaction without HCl. When the reaction is carried out at 222-230 °C, increasing the reaction time doesn't have a significant impact on the conversion of 9-hydroxynonanoic acid. It was also found that under melt condensation reaction conditions, intermolecular reactions of 9-hydroxynonanoic occurred, as a result, chain ester products were the primary products obtained instead of lactones. In addition, it was found that some azelaic esters maybe be formed at high temperatures indicating that 9-hydroxynonanoic acid or the lactones may be further oxidized.

Table 8. Melt condensation of 9-hydroxynonanoic acid under different reaction temperatures and conditions and comparison of their conversion

Entry No.	Reaction conditions	Reaction time(hour)	Conversion of 9-hydroxynonanoic acid to chain esters[c]
Exp.1	96 °C and [a]	2.0	17.15 %
Exp.2	96 °C, (HCl, 5.0 %) [a]	2.0	45.71 %
Exp.3	124-126 °C [b]	2.0	70.12 %
Exp.4	154 °C [b]	2.0	80.17 %
Exp.5	222-230 °C [b]	2.0	89.40 %
Exp.6	222-230 °C [b]	4.0	88.60 %
Exp.7	220-223 °C [b]	2.0	90.00 %

[a]: the pressure inside the reaction system was 30 Torr

[b]: the pressure inside the reaction system was 0.35 Torr.

[c]: detected by ^{1}H NMR

3.4.2 Attempt to synthesize nonanolactone using different catalysts

A few different methods were tried in an attempt to synthesize nonanolactone from 9-hydroxynonanoic acid. The reaction conditions are shown in Table 9. As seen from Table 9, different acid catalysts were tried including HCl, BF_3 and *p*-TsOH, however, a complex mixture of products was obtained. It was found that the obtained mixture contained chain esters in all the cases. This could be due to difficulties in the formation of 9 membered rings because of ring strain and instead aliphatic chain esters are formed instead. DCC and cyanuric chloride were also tried to form the lactone; however, no nonanolactone was observed in both cases.

3.4.3 Hafnium chloride catalyzed synthesis of the dilactone

When hafnium chloride (a commercially available reagent) was used to catalyze the lactonization reaction of 9-hydroxynonanoic acid in xylene under refluxing conditions, a dilactone product was obtained with high yield and high purity (98 %). The mechanism of this reaction is shown in Figure 20 and 21.

In an attempt to optimize the reaction, different solvents were tested. First, THF was tried as a solvent and the reaction was carried out in refluxing conditions. However, it was found that even after 24 hours, no obvious further product was observed. Instead, there was mostly starting material remaining. This could be due to the fact that THF has a relatively low boiling point (approx. 66 °C), and at this temperature, trace amounts of

Table 9. Attempted synthesis of nonanolactone[a] using different reaction conditions (catalyst, temperature and reaction time)

Starting material	Catalyst	Temperature (°C)	Reaction time (hours)	Conversion to chain ester mixtures[b] (%)
9-HNA	Conc. HCl (20 mol %)	45	24	17
9-HNA	Conc. HCl (50 mol %)	45	24	90
9-HNA	BF_3-CH_3OH (20 mol %)	20	24	0
9-HNA	*p*-toluenesulfonic acid (20 mol %)	80	24	30
9-HNA	Cyanuric chloride	25	8	80
9-HNA	DCC (20 mol %)	25	12	20

a: No nonanolactone was obtained, instead, chain ester mixtures were procured.

b: Conversion of 9-hydroxynonanoic acid was identified by ^{1}H NMR.

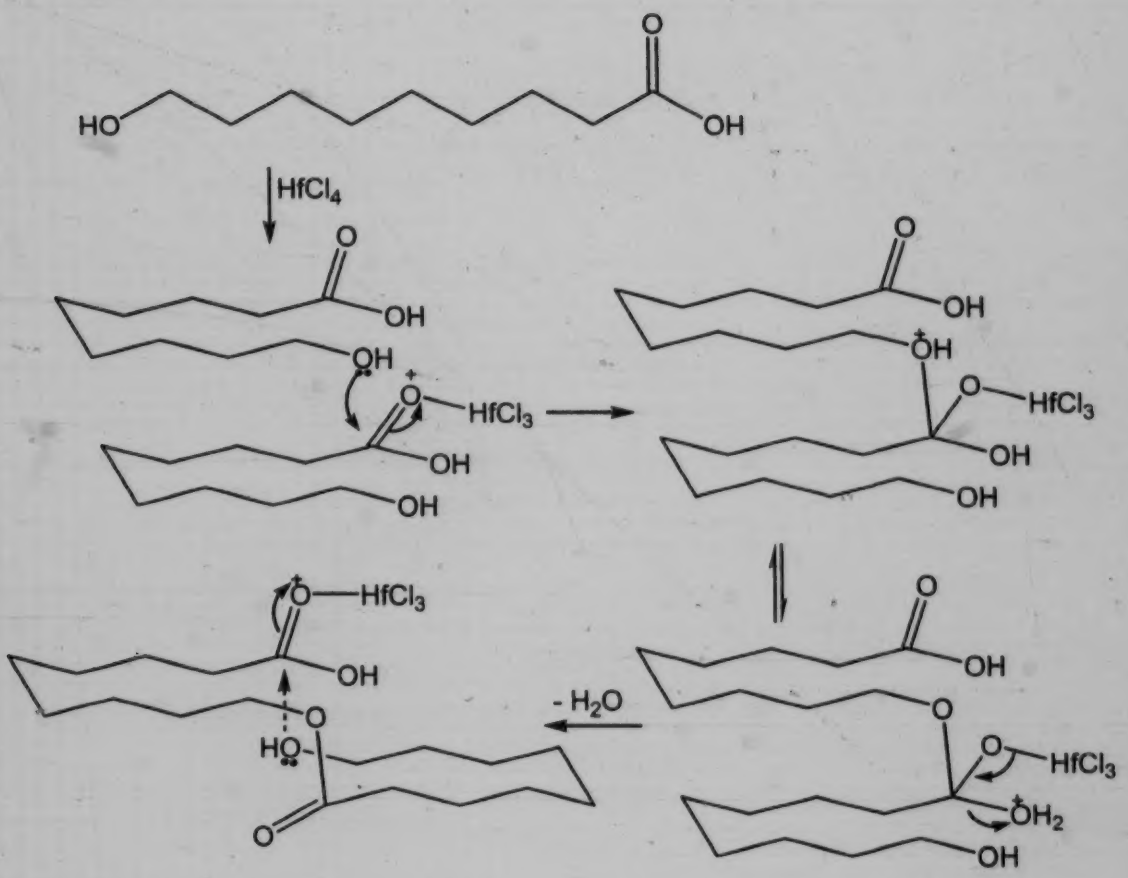


Figure 20: Mechanism of formation of dilactone under hafnium chloride catalysis

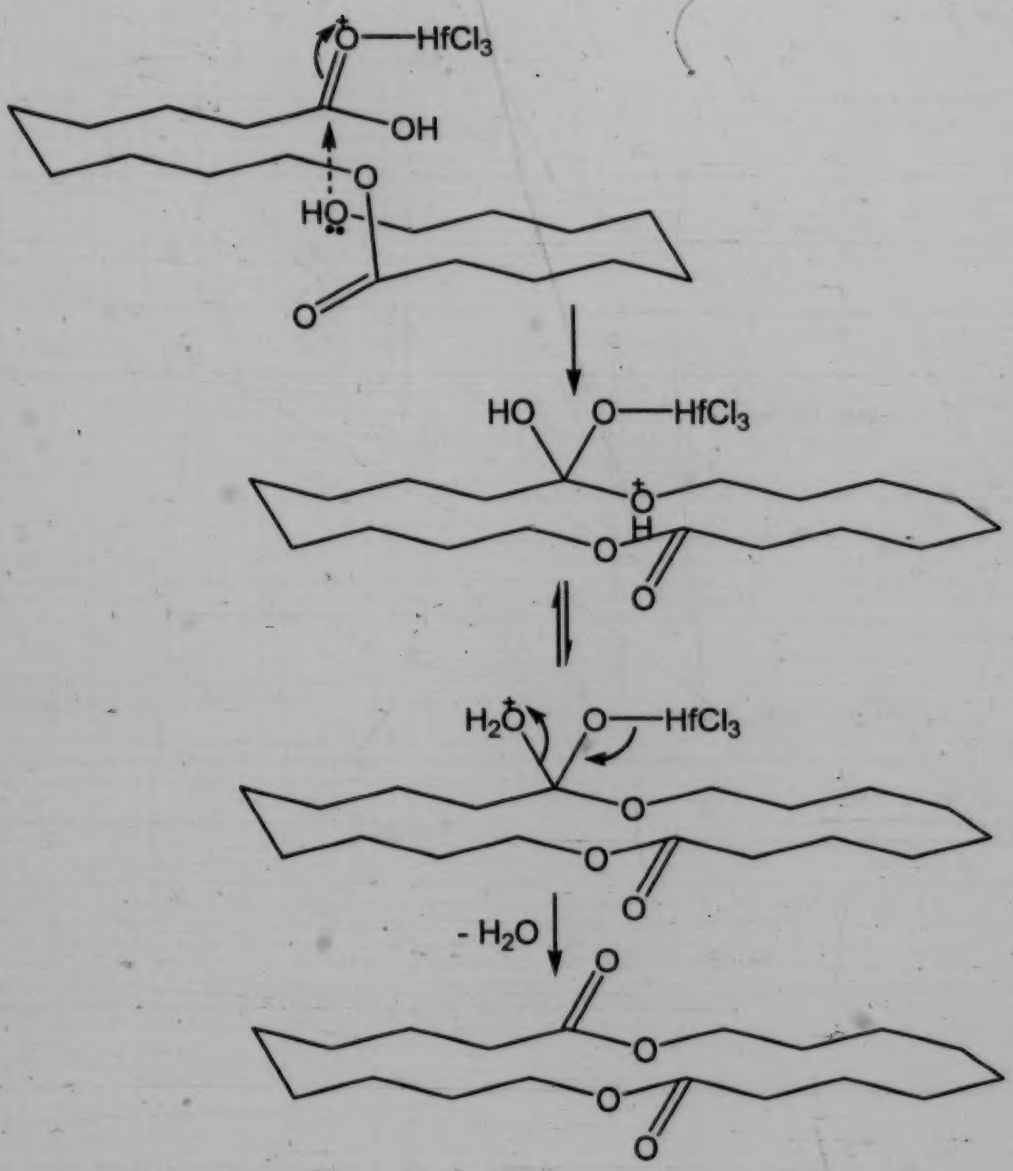


Figure 21: Mechanism of formation of dilactone under hafnium chloride catalysis

(continued)

water cannot be distilled from the reaction mixture to drive the reaction forward. This could be regarded as the rate-limiting step. In order to find a more suitable solvent, high boiling solvents such as xylene and toluene were tested. In both cases, the dilactone was produced in high yields of 98 %. As xylene and toluene both have high boiling points (above 110 °C), it can efficiently azeotrope with water produced in the reaction. The 3Å molecular sieves used in the reaction can absorb the water efficiently, thus, driving the reaction forward to form the dilactone. Different reaction conditions were tried. Details of the different reaction conditions are summarized in Table 10.

3.4.4 Structure identification of the dilactone

The structure of the dilactone obtained after the 24 hour reaction was identified by analysis with FTIR, ^{1}H NMR, ^{13}C NMR and GC-MS.

According to the FTIR spectrum which is shown in Figure 22, there is a very sharp peak at 1733 cm^{-1}. This corresponds to the ester carbonyl functionality of the dilactone. The peaks at 2853 cm^{-1} and 2929 cm^{-1} correspond to the symmetrical and asymmetrical vibration of the methylene group. The absorption at approximately 1160 cm^{-1} and 1216 cm^{-1} correspond to the –C-O-C- symmetrical and asymmetrical vibrations.

GC-MS analysis (EI / 70 eV) was carried out using an HP-5 column. The GC-MS spectrum as shown in Figure 23 shows only one peak with a retention time of 19.2 minutes. The spectrum indicates that the sample is very pure. According to the GC-MS fragmentation pattern as shown in Figure 24, it was found that the molecular ion (M^{+}) of the peak was 312 and it should be noted that no other peaks were observed after

Table 10. Synthesis of dilactones under different reaction conditions and comparison of their yields

Entry No.	$HfCl_4$	Solvent	Time/ hour	Yield [a]
1	2 mol %	Xylene, reflux	24/48	98 %
2	2 mol %	Xylene, reflux Low conc.	24	96 %
3	2 mol %	Toluene, reflux	24	98 %
4	2 mol %	THF, reflux	24	No product was detected

[a]: Yields are as a percentage of theoretical yield.

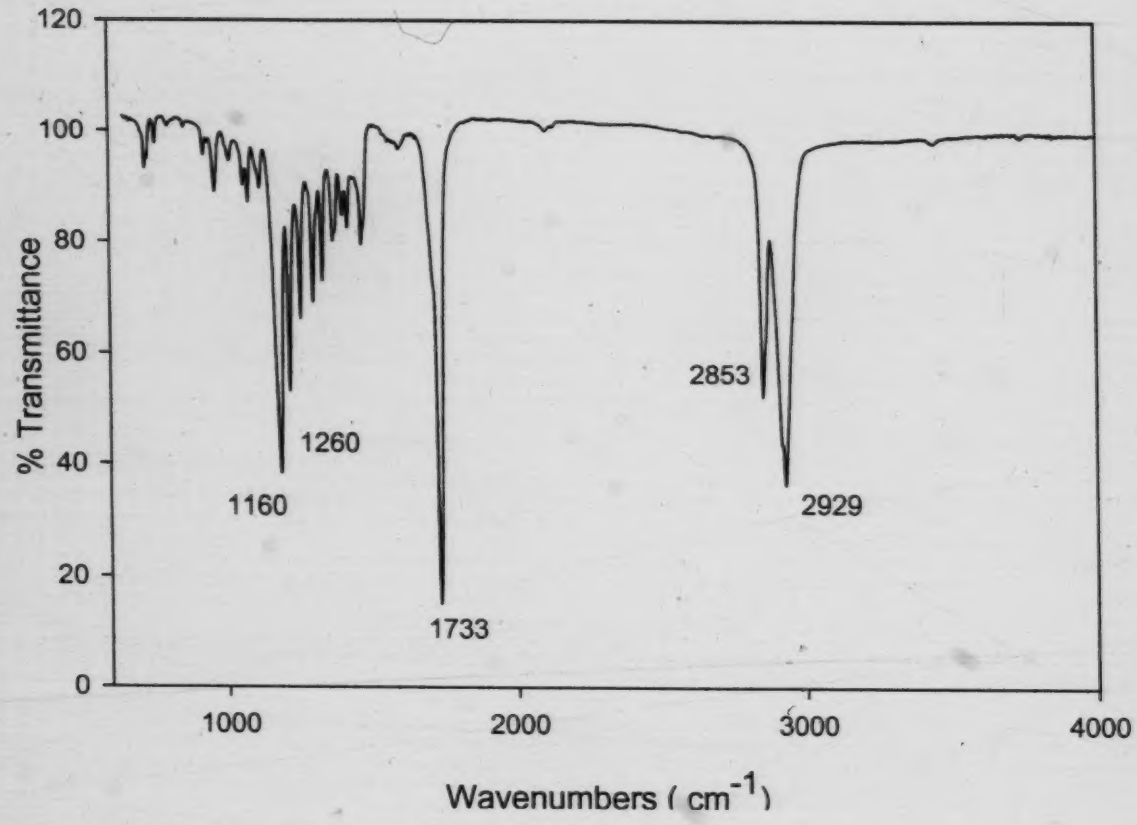


Figure 22: FTIR spectrum of the dilactone

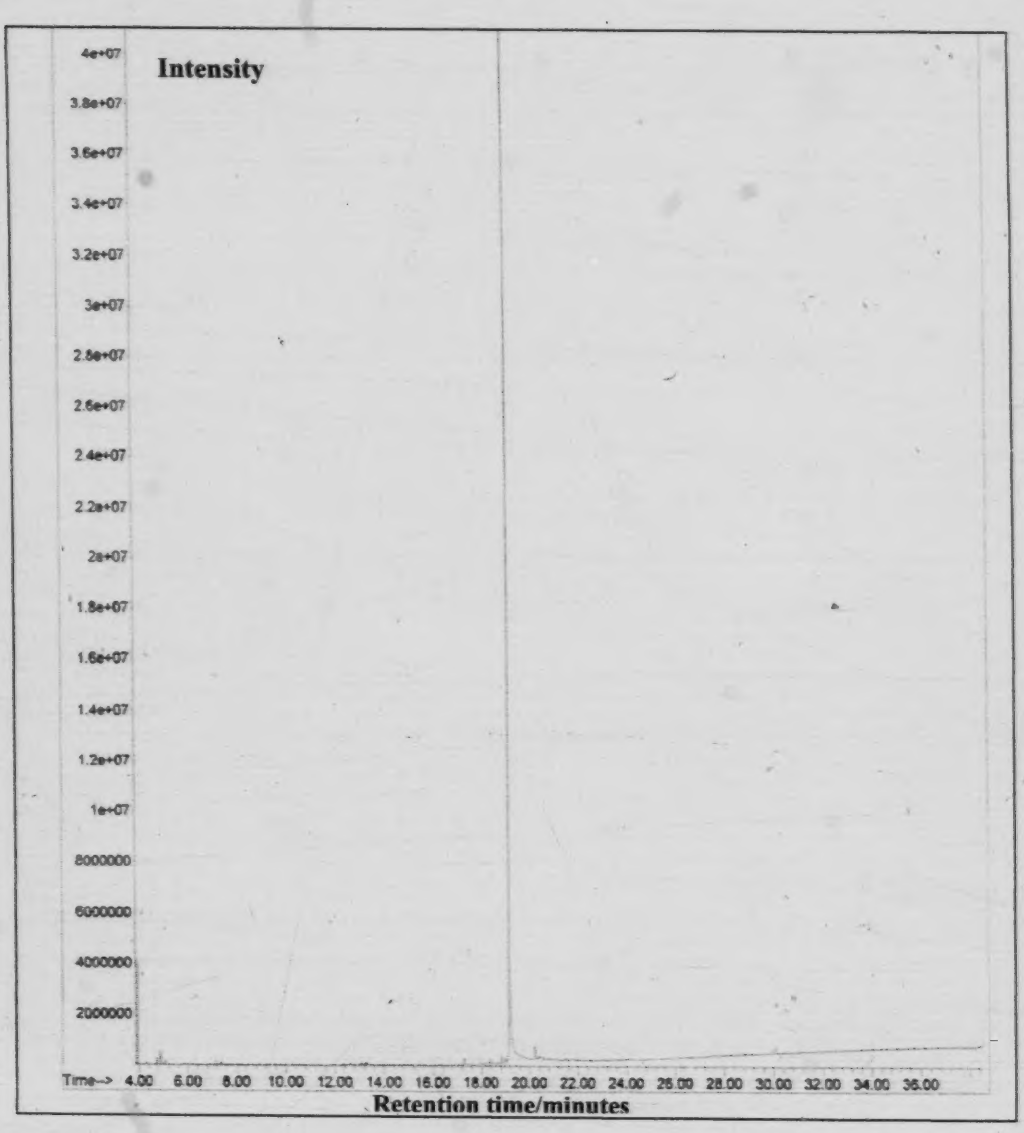


Figure 23: GC-MS chromatogram of the dilactone

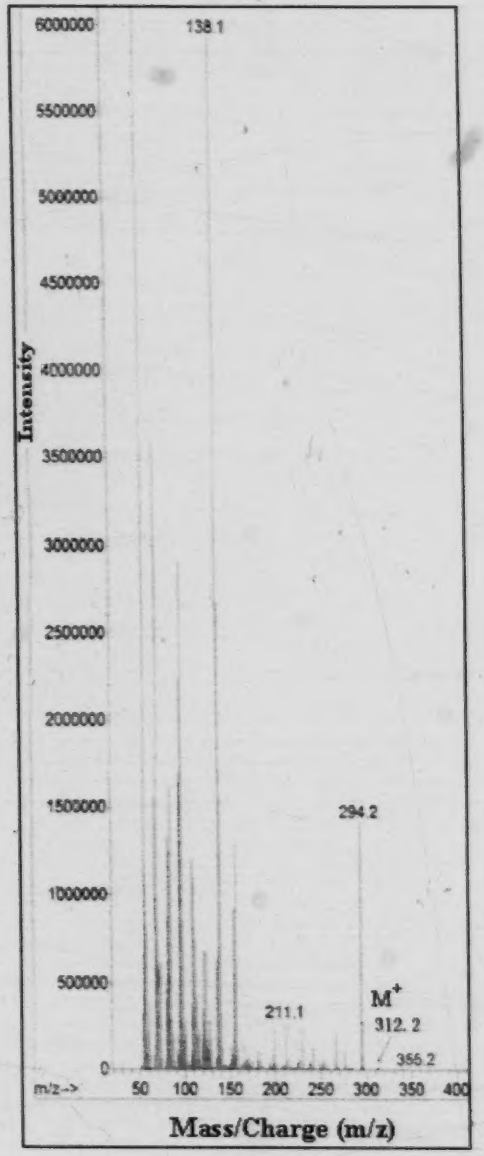


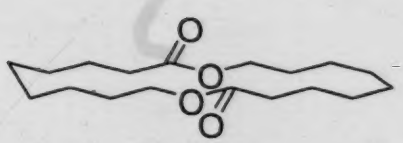
Figure 24: GC-MS spectrum showing the fragmentation pattern of the dilactone

m/z 312. The peak at 294 corresponds to a loss of one molecule of water (M^+-18). These fragmentation patterns (shown in Figure 24) were consistent with the published literature (31).

According to the ^{1}H NMR spectrum of the dilactone, the structure was confirmed to be that shown in Figure 25. Figure 26 shows the proton NMR spectrum of the dilactone. It can be seen that the multiplet with a chemical shift of approximately 1.30 ppm corresponds to sixteen methylene protons (16 H, -C$\underline{H}_2$C$\underline{H}_2$CH$_2$CH$_2$COO-). The multiplet at approximately 1.60 ppm corresponds to the other eight methylene protons (8 H, -C$\underline{H}_2$CH$_2$COO- and –COOCH$_2$C$\underline{H}_2$-) and the triplet with a chemical shift of 2.30 ppm is indicative of the protons adjacent to a carbonyl functionality (4 H, t, J = 7.2 Hz, -C$\underline{H}_2$COO-). Finally, the triplet with a chemical shift of 4.07 ppm corresponds to the protons adjacent to the ester functionality (4 H, t, J = 6.8 Hz, -COOC$\underline{H}_2$-).

According to the ^{13}C NMR spectrum shown in Figure 27, the peaks occurring between 24.94 ppm and 34.33 ppm correspond to the methylene carbons that are situated the furthest away from the carbonyl and ester functional group. The peak at 64.35 ppm corresponds to the methylene group (-COO$\underline{C}$H$_2$-) that is directly attached to the ester functional group and the signal at 173.90 ppm corresponds to the carbon of the carbonyl functional group (-CH$_2\underline{C}$OOCH$_2$-).

According to the 2D COSY spectrum as shown in Figure 28, three correlations were observed. Protons in peak A and B have a correlation, the protons in peaks B and C have a correlation and the protons in peaks C and D have a correlation. The 2D COSY spectrum confirms the structure of the dilactone.



Dilactone

Figure 25: Confirmed structure of the dilactone

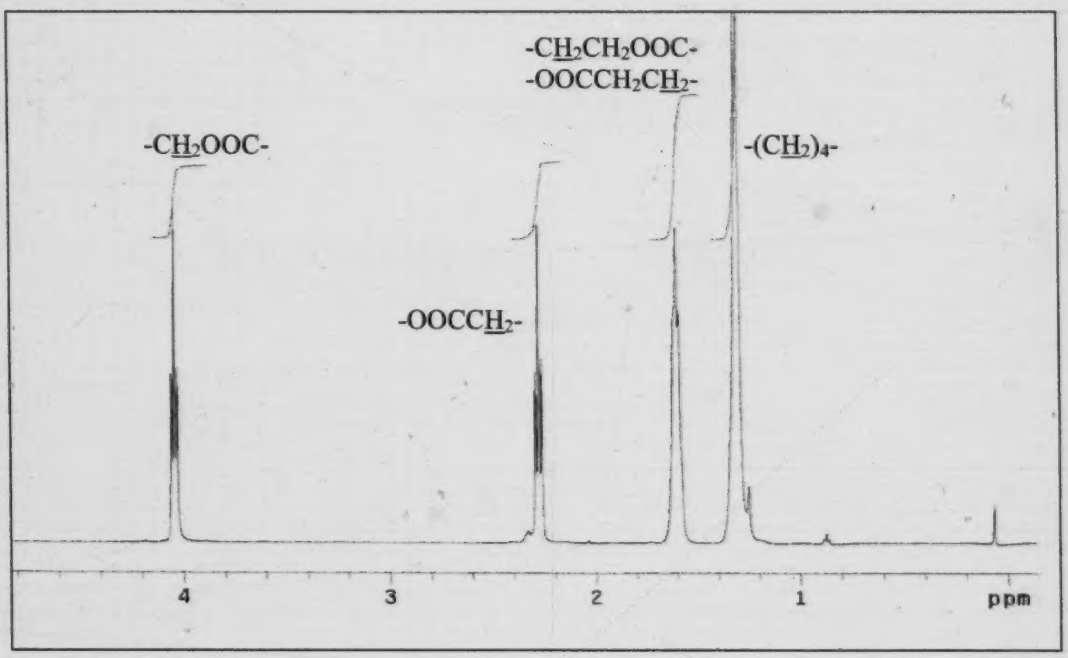


Figure 26: ^{1}H NMR spectrum of the dilactone

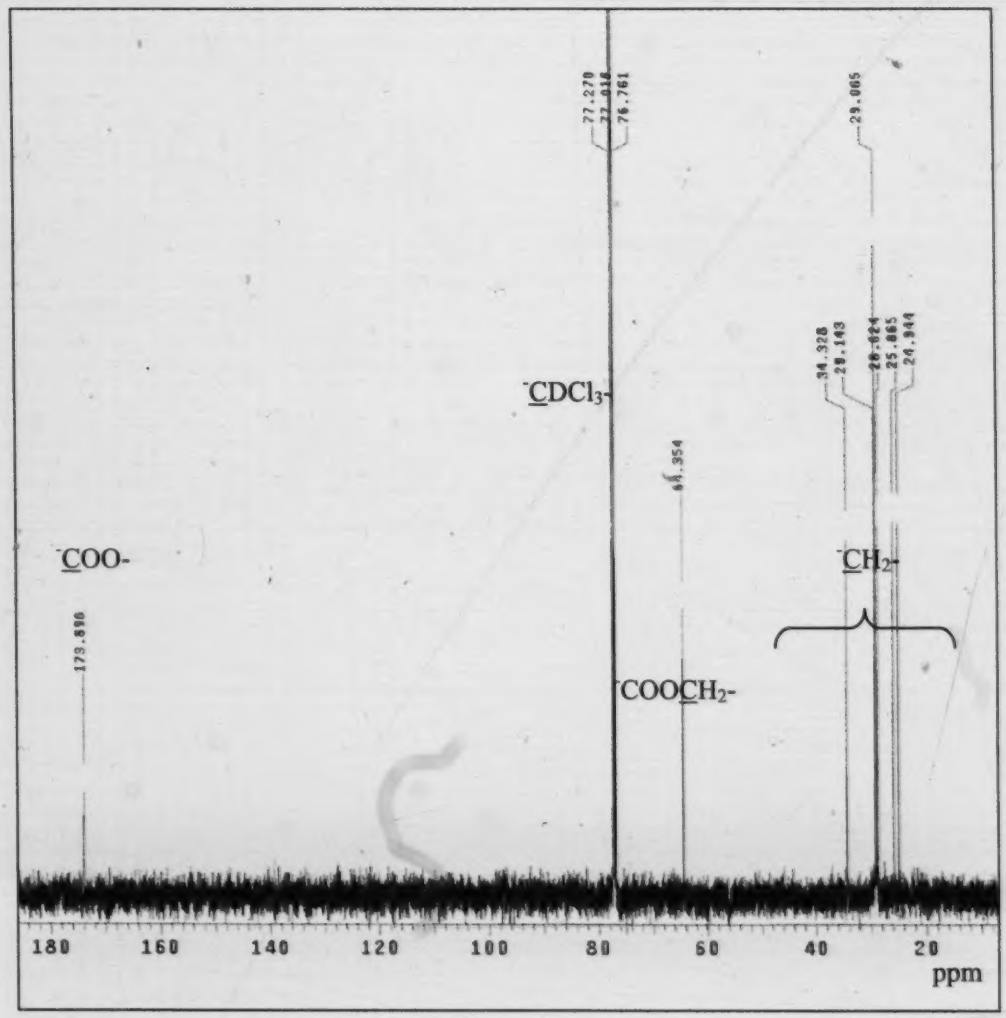


Figure 27: ^{13}C NMR spectrum of the dilactone

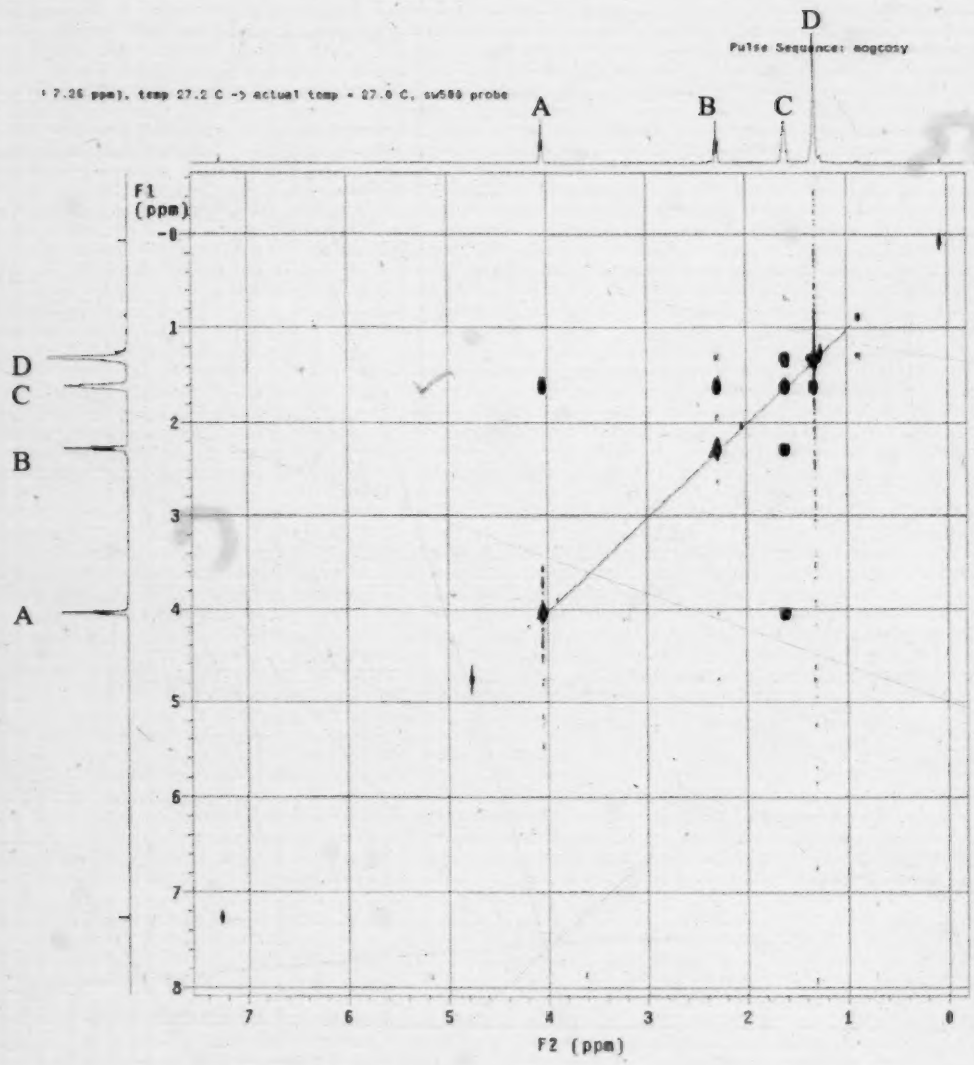


Figure 28: 2D COSY of the dilactone

Here are the spectra data of dilactone: *FTIR*, (Solvent was $CDCl_3$) 1733.0 cm^{-1}, 2853 cm^{-1}, 2929 cm^{-1},1160 cm^{-1} and 1216 cm^{-1}. *GC-MS*: (EI / 70 eV) Retention time 19.2 minutes, molecular ion (M^+) was 312. Fragment of 294 (which was obtained when the whole molecular lost water (H_2O, 18)) and 138 (which was obtained from 294 when lost a fragment of 156) matched the fragmentation that was reported in the literature. (31) *^1H NMR* (400 MHz, $CDCl_3$): δ, 1.30 (16 H, -C$\underline{H_2}$C$\underline{H_2}$CH_2CH_2COO-), 1.60 (8 H, -C$\underline{H_2}$CH_2COO- and –COOCH_2C$\underline{H_2}$-), 2.30 (4 H, t, *J*=7.2 Hz, -C$\underline{H_2}$COO-), 4.07 (4 H, t, *J*=6.8 Hz, -COOC$\underline{H_2}$-). *^{13}C NMR* (100 MHz, $CDCl_3$): δ ppm, 24.94, 25.87, 28.62, 29.07, 29.14, 34.33, 64.35 (-COO$\underline{C}H_2$-), 173.90 (-C$H_2\underline{C}$OOCH_2-). *2D H-H COSY* spectrum of dilactone indicated that peak A and peak C have a correlation, peak B and peak C have a correlation, and peak C and peak D have a correlation, which matched the structure of dilactone.

3.5 Synthesis of polyesters

Polyesters A, B and C were synthesized by ring opening polymerization reactions of the dilactone monomer catalyzed by lanthanum chloride and aluminium isopropoxide.

3.5.1 Reaction mechanism for the formation of polyesters

The reaction mechanism for the formation of the polyester catalyzed by aluminium isopropoxide is shown in Figure 29. The reaction involved 3 steps. The first

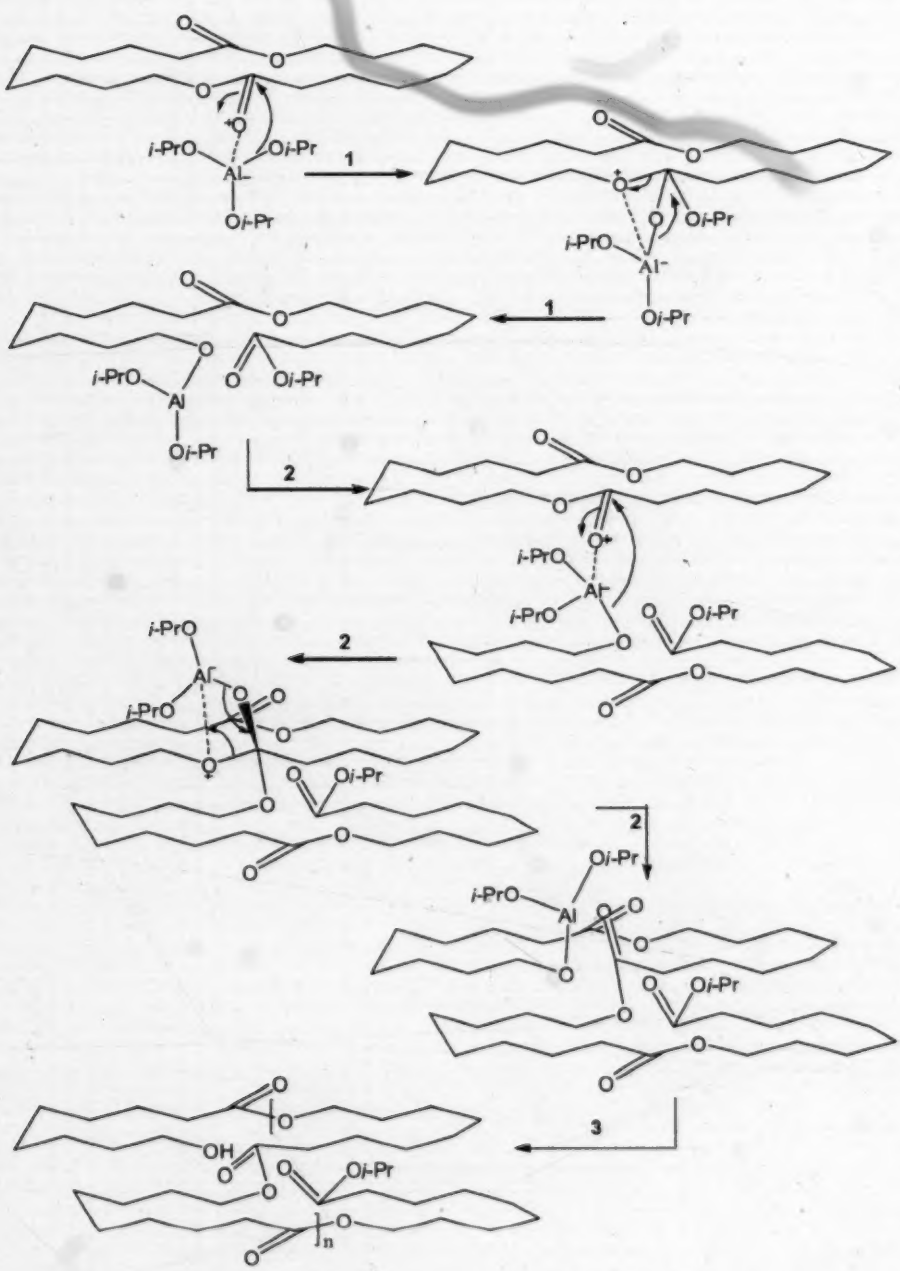


Figure 29: Reaction mechanism for polyester synthesis catalyzed by Al (O*i*-Pr)$_3$

step (1) is an initiation step; aluminium coordinates to the carbonyl group and forms a complex, thus activating the carbonyl group. In the second step, a free hydroxyl group attacks the carbonyl and increases the length of the polymer chain, which is also termed a propagation step. In the third step known as the termination step, HCl is used to quench the reaction and a polyester is obtained with two different terminal functional groups (at one end is an isopropyl group and at the other is a hydroxyl group). The mechanism of polyester synthesis catalyzed by lanthanum chloride and lipase catalyst has already been discussed in the introduction chapter. Use of lanthanum chloride and lipase CA to catalyze the ROP reaction (discussed earlier) allows for the formation of polyesters with terminal hydroxyl and carboxylic acid functionalities.

3.5.2 Structure characterization

Structures of the polyesters obtained via ROP were determined by ^{1}H NMR and FTIR are shown in Figure30 and Figure 31. According to the terminal functional groups, polyesters were formed when catalyzed by different catalysts. Polyesters A, B and C were obtained from ring opening polymerization reactions of the dilactone catalyzed by lanthanum chloride, aluminium isopropoxide and lipase CA, respectively. In the ^{1}H NMR spectra of both polyester A and C, there is a triplet at 3.65 ppm that corresponds to the methylene group adjacent to the hydroxyl group. The hydroxyl groups in the above two polyesters are the terminating groups and indicate that the polyester was formed. In the ^{1}H NMR spectrum of polyester B, the signals at 3.65 ppm and 5.05 ppm have an

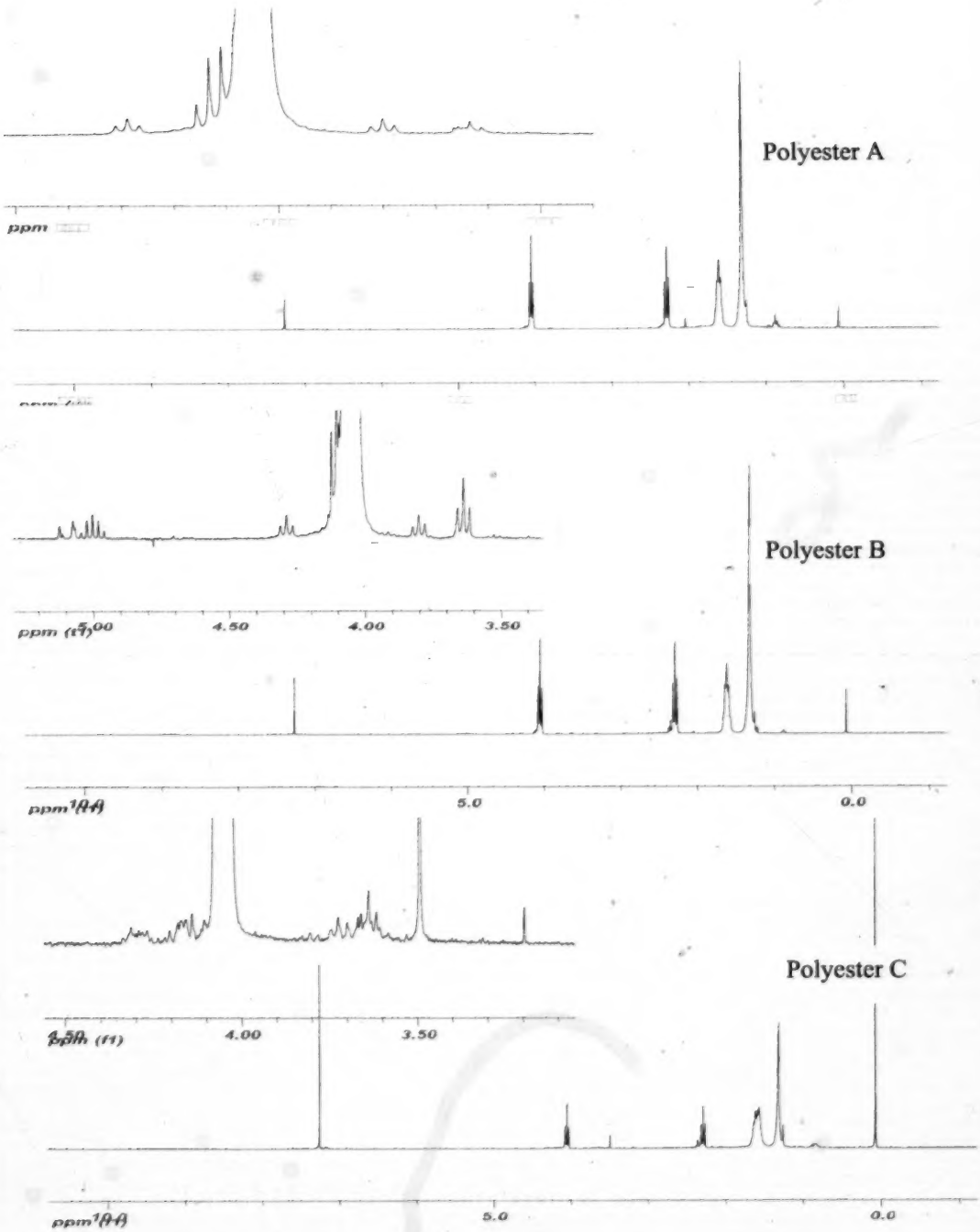


Figure 30: ^{1}H NMR of polyesters synthesized by different methods

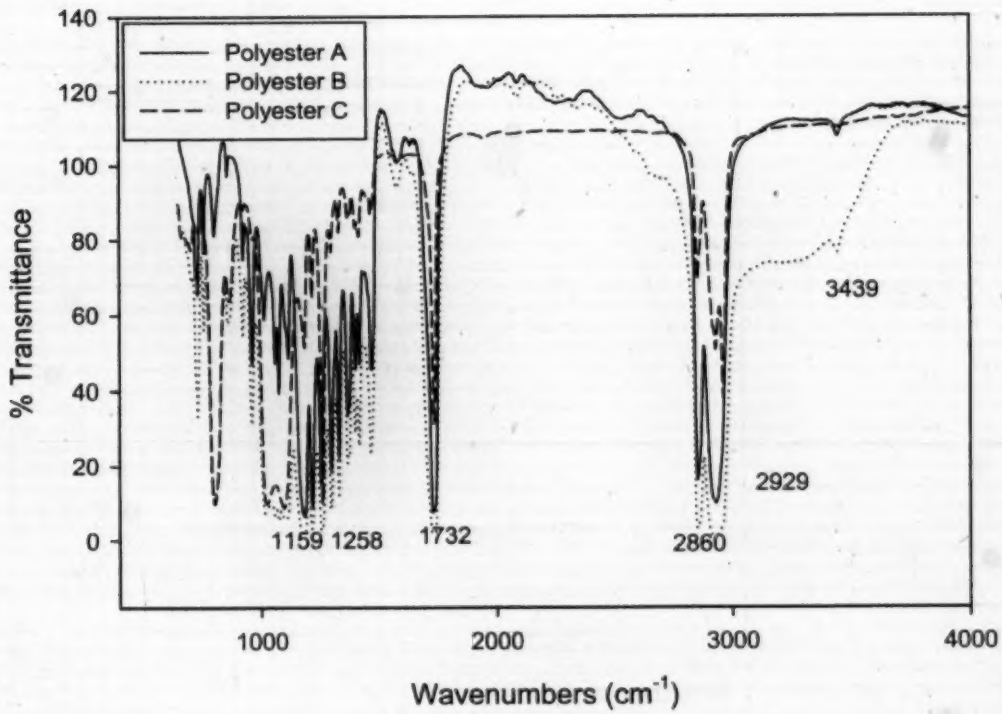


Figure 31: FTIR spectra of polyesters A, B and C

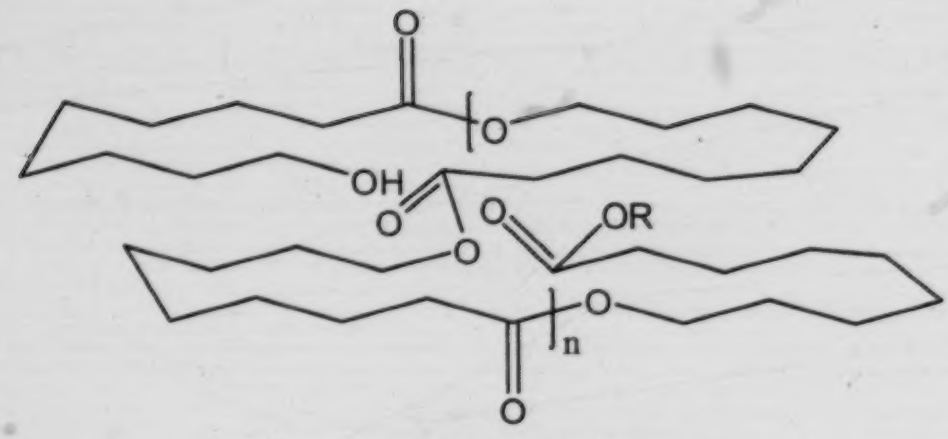
integration ratio of 2 and correspond to the methylene group (-C<u>H</u>$_2$OH, triplet) adjacent to the hydroxyl group and the isopropyl ester group (CH_3)$_2$C<u>H</u>-OCO-, septuplet), both of which are terminating groups. These terminal groups indicate that the polyesters were formed.

FTIR spectra of the polyesters A, B and C are shown in Figure 31. From the spectra, it can be seen that all of the above have a strong absorption band at approximately 1730 cm^{-1} which corresponds to the carbonyl group. For the polyesters A, B and C, both show absorption band around 3439 cm^{-1}, which corresponds to the terminal hydroxyl group of the polyester chains. The structures of the polyesters are shown in Figure 32.

3.5.3 Physical properties

The number average molecular weights (M_n) of the polyesters were determined by ^{1}H NMR end group analysis (70) and GPC. The results are listed in Table 11. On average, M_n, determined by ^{1}H NMR end group analysis was slightly lower than the values obtained by GPC, but the trends were the same. The M_n of polyester A was higher than that of polyester B.

Thermal behaviours of both polyesters were characterized by MDSC. The melting profiles of polyester A and polyester B are shown in Figure 33. A weak glass transition was observed for polyester B, whereas no obvious glass transition was observed for polyester A. This might be due to the fact that heat capacity change over the glass transition region of these types of materials was too small to be detected.



R= H Polyesters A and C
R=$CH(CH_3)_2$ Polyester B

Figure 32: Structures of polyesters A, B and C

Table 11. Physical properties of polyesters A and B

	M_n (g/mol)	M_w (g/mol)	PDI	T_g (°C)	T_m (°C)	ΔH_f (J/g)	W_c (%)
polyester A	7000 [a]/4200 [b]	10000 [a]	1.4 [a]	—	69.2 ± 0.1	33 ± 2	16 ± 1
polyester B	5300 [a]/3600 [b]	8000 [a]	1.5 [a]	- 42.3 ± 0.2	69.1 ± 0.2	39 ± 2	19 ± 1

Polyester A: Catalyzed by lanthanum chloride

Polyester B: Catalyzed by aluminium isopropoxide

a: Obtained from GPC.

b: Calculated by ^{1}H NMR.

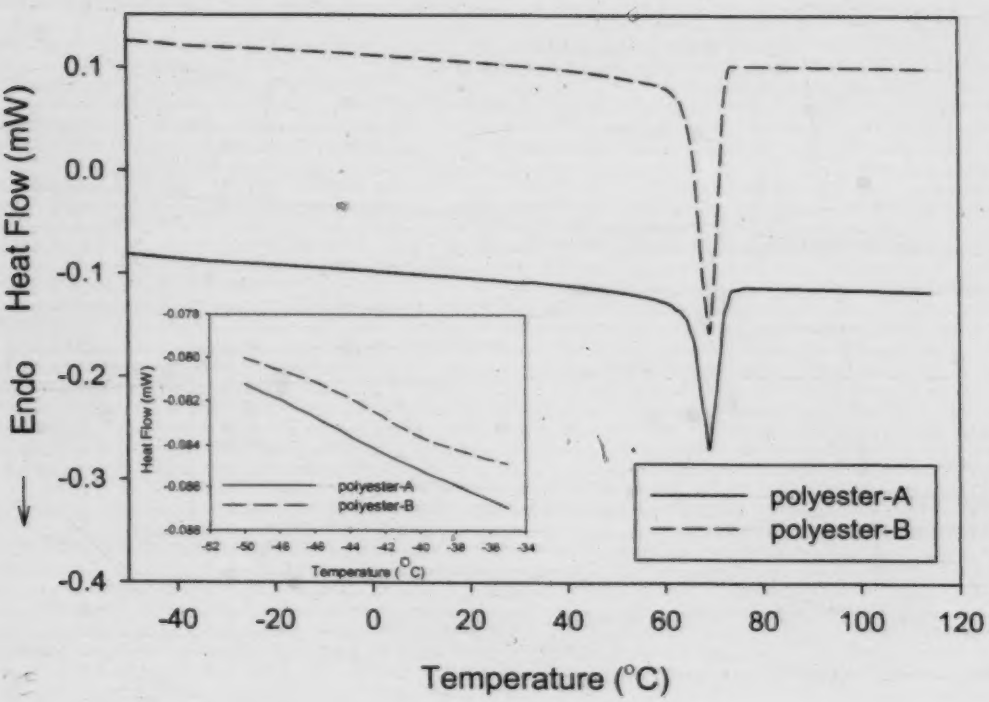


Figure 33: Melting profiles of polyester A and polyester B

From Figure 33, the melting point, T_m and heat of fusion, ΔH_f of each product were determined and summarized in Table 11. T_m of polyester A is slightly higher than that of polyester B, while ΔH_f and w_c of polyester A are slightly lower than those of polyester B. These results suggest that these two polyesters have similar thermal behaviour. In addition, the w_c s of both polyesters is much lower than that of the dilactone starting material (36 %). This could be due to the fact that small chains generate more regular crystal packing with small portions of amorphous material. On the other hand, polymers with long chains cannot be accommodated effectively into the crystals, and therefore have a large portion of chains in the amorphous phase resulting in lower crystallinity.

TGA curves of the two polyesters and their derivatives (DTGA) are shown in Figures 34 and 35, respectively. All the decompositions started at approximately 250 °C, losing weight very slightly until 300 °C, where a rapid drop followed and ended at approximately 500 °C. The shapes of the weight loss curves of both polyesters were similar in the temperature range of 250-410 °C and different in the 410-500 °C temperature range.

DTGA data reveal three main degradation processes, one correlated with the first 10-20 % of the weight loss, the second with the 70-80 % of the weight loss and the third with the remaining weight loss. Polyester A had its fastest rate of loss at 380 °C, and polyester B had its fastest rate of loss at 390 °C.

According to the thermal degradation mechanism of P (ε -CL) (94, 101) which has similar structure with the polyesters A and B, the first stage of decomposition might

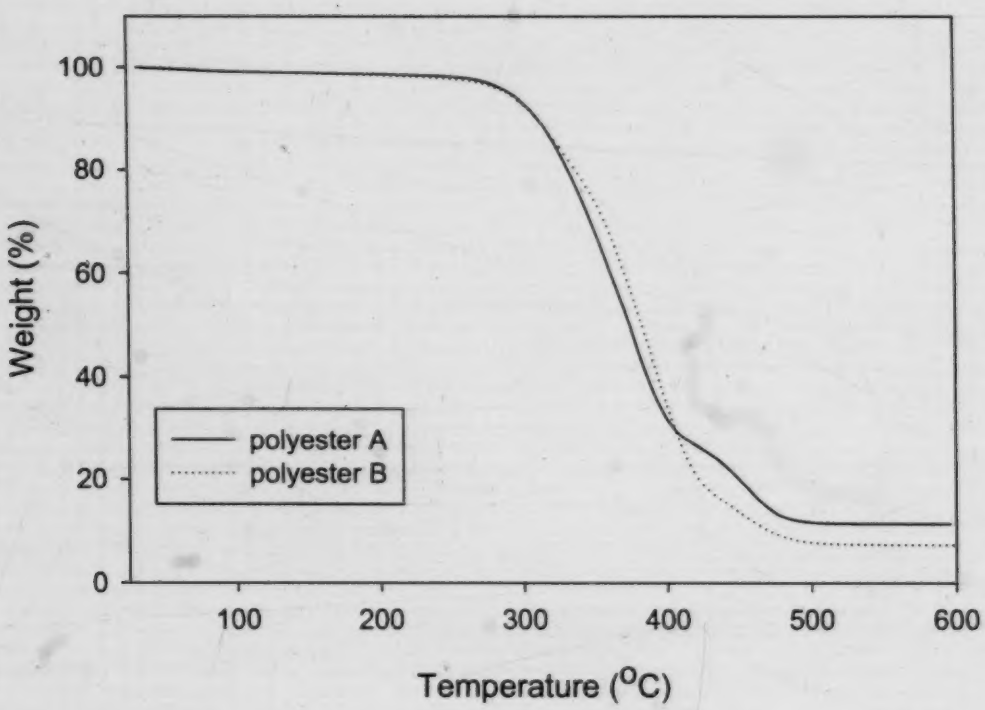


Figure 34: TGA data for polyesters A and B

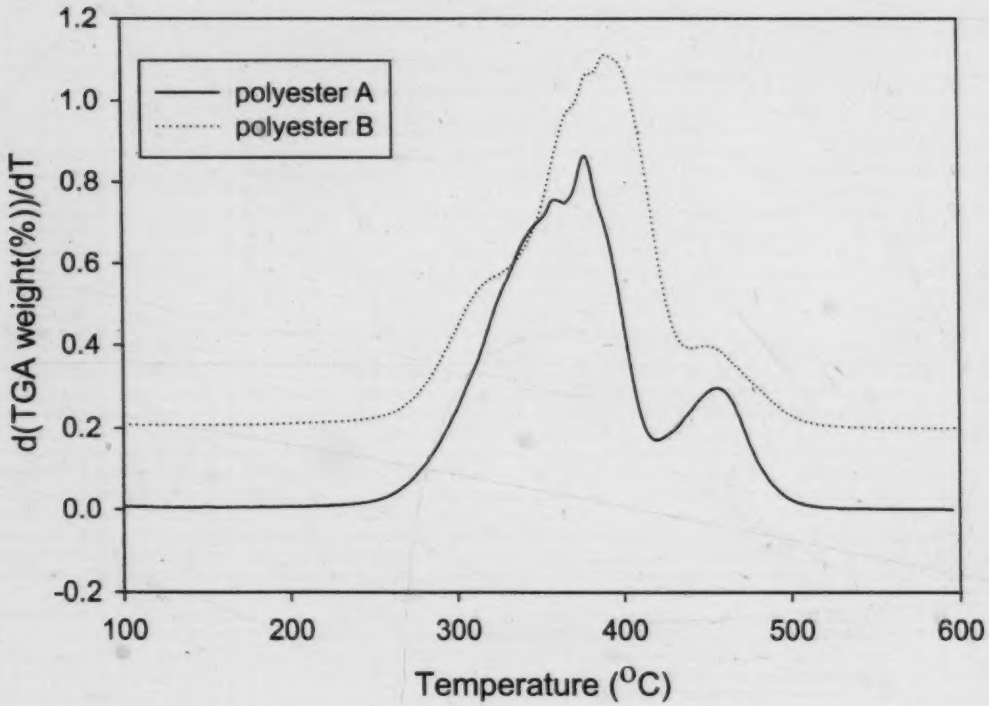


Figure 35: DTGA data for polyesters A and B

be due to oligomer degradation and the random degradation of ester chains. The second step of decomposition might result from volatile products such as water and carbon dioxide. The third step of decomposition could be caused by depolymerization of the polymer chain *via* an unzipping mechanism, which requires the presence of a hydroxyl group in order to occur. The degradation tendency of polyesters A and B is similar to that of the P (ε -CL) as shown from the TGA and DTGA curves. Slightly different degradation features might result from the different terminal groups of these two polyesters. As the terminal groups in polyester A are a hydroxyl group and carboxylic acid group, while the terminal groups in polyester B are a hydroxyl group and an isopropyl group.

Chapter 4 Conclusions

9-Hydroxynonanoic acid:

9-Hydroxynonanoic acid can be synthesized from oleic acid, methyl oleate and polyols of canola oil using ozonolysis and hydrogenation reactions. A 28 % yield of 9-hydroxynonanoic acid was obtained when oleic acid was used as a starting material. A 74 % yield of highly pure 9-hydroxynonanoic acid was obtained after recrystallization when methyl oleate was used as the starting material. A 58 % yield of 9-hydroxynonanoic acid (purification by silica gel chromatography) was obtained when polyol mixtures were used starting materials.

It was found that a protic solvent system such as ethanol is a good solvent system for the synthesis of 9-hydroxynonanoic acid from methyl oleate.

Nonanolactone (monolactone):

A few cost efficient methods were tried in order to synthesize nonanolactone. However it was found that instead of nonanolactone being formed, some chain ester oligomers were obtained instead.

1,11-Dioacycloicosane-2,12-dione (dilactone):

It was the first time that 1,11-Dioacycloicosane-2,12-dione (dilactone) was synthesized in high yield (98 %) and high purity (98 %) *via* an intramolecular condensation reaction of 9-hydroxynonanoic acid catalyzed by hafnium chloride. This

method has been found to be suitable for scale up synthesis. It was found that xylene was the optimal solvent for the synthesis of the dilactone.

Polyesters:

Polyesters have been produced by ring opening polymerization of 1,11-dioacycloicosane-2,12-dione (dilactone) catalyzed by 3 different catalytic systems: 1) aluminium isopropoxide, 2) lanthanum chloride and 3) lipase CA. The number average molecular weights of the polyesters range from 8000 to 10000, as determined by GPC. It was found that aluminium isopropoxide and lanthanum chloride were the most cost efficient catalysts (of the three methods) for these ROP reactions, while lipase CA was more expensive and took a longer time to yield the polyester products. In addition, for the aluminium isopropoxide catalyzed reaction, using THF as the solvent did not produce any desired product but using toluene as the solvent, the desired products were obtained.

No obvious T_g was observed for the polyesters. This might due to the following reasons: 1) The heat capacity change over the glass transition region of these types of materials is too small to be detected; 2) Additional phenomenon which occurs near the glass transition region affected the determination of its existence.

T_ms of both polyesters are 3°C higher than the dilactone starting material, while ΔH_fs of these polyesters are about 50 J/g lower than the dilactone starting material. This data suggests that these two polyesters have similar thermal behaviour.

Chapter 5 Future work

The methodologies that have been developed to produce 9-hydroxynonanoic acid can also be applied to free fatty acid material recovered from soapstock and deodorizer distillates (the waste from canola oil refining).

5.1 Components of soapstock and deodorizer distillates

Soapstock and deodorizer distillates are the major by-products obtained from vegetable oil refining, and both are mostly wet lipidic mixtures. Research on soapstock was first carried out in the mid-nineteen fifties (102, 103). At that time, the composition of soapstock was determined based on acid and iodine values, unsaponifiable matter content, volatile matter content, free fatty acid content and neutral oil and ash content. In the following years, further research was carried out on different kinds of soapstock. In 1987, the first attempt to characterize soapstock was achieved by Waliszewski and coworkers (104). Following this success, other research groups such as Dowd (105, 106) and Durant (107, 108) have described methods to also characterize soapstock and deodorizer distillates of canola oil and contents of unsaturated fatty acids; these were shown in Tables 12 and 13.

5.2 Use of unsaturated fatty acids from soapstock and deodorizer distillates

The unsaturated fatty acids recovered from soapstoack and deodorizer distillates, such as oleic acid, linoleic acid and linolenic acid (Structures shown in Figure 9) contain

Table 12. Fatty acid contents of different soapstocks

	Content (%) Report on a dry basis			
Fatty acids	Cotton seeds (Dowd, 1996)	Corn (Dowd, 1998)	Peanut (Dowd, 1998)	Canola (Durant *et al.*, 2006
Myristic acid	0.24	0.031	0.066	Nd
Palmitic acid	9.31	8.62	8.62	4.63
Palmitoleic acid	0.18	Tr	Tr	0.15
Stearic acid	0.96	0.507	0.458	Nd
Oleic acid	6.07	9.36	11.6	**15.57**
Linoleic acid	16.50	17.8	7.75	**3.31**
Linolenic acid	nd	Nd	Nd	**0.24**
Arachidic acid	0.077	0.076	Tr	0.12

nd=not detected, tr=trace amount.

Table 13. Components of canola oil deodorizer distillate samples quantified by GC-MS

Components	Concentration (g/100g sample)	R. S. D. (%)
Lauric acid	0.04	7.47
Myristic acid	0.17	9.51
Palmitic acid	4. 74	3.76
Palmitoleic acid	0.14	7.85
Oleic acid	**60.20**	1.07
Linoleic acid	**1.94**	2.05
Linolenic acid	**0.29**	6.55
Arachidic acid	0.11	5.58
Monoolein	0.41	14.09
Monolinolein	0.09	4.67

Concentration (g/100g sample) reported on a dry basis. N=3 replicates. R. S. D., relative standard deviation (n=3). R. S. D. of the internal standard is 4.74 %.

alkene functional groups between carbons 9 and 10. They can be readily converted into the corresponding methyl esters, which are more renewable starting materials for producing 9-hydroxynonanoic acid. Thus, the methodology applied in the synthesis of 9-hydroxynonanoic acid using the methyl oleate as a starting material can also be applied in the ester mixtures of these unsaturated fatty acids in an attempt to produce value added products from these renewable sources.

According to the literature (107, 108) reported by Durant in 2006, more than 19.12 % of unsaturated fatty acids can be recovered from canola soapstock (shown in Table 12), and more than 64.23 % of unsaturated fatty acids can be recovered from deodorizer distillate samples (shown in Table 13).

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